

REMARKS

Applicants acknowledge that claims 1-28, 54-58, 60 and 61 are withdrawn as being directed to a non-elected invention.

By the present amendment, claims 1-28, 54-58, 60 and 61 are canceled. Claim 53(g) is amended to correct the obvious error to formula (7) and claim 59 is amended to correctly refer to composition claim 29. Amended formula (7) corrects an obvious error. Amended formula (7) differs from former formula (7) by deletion of the hydrogen atom formerly depicted as bound to the nitrogen atom along with the $-(R^8)_n-$, $-(R^6)_y-$ and $-R^4-$ moieties. As formerly depicted, a quaternary amine (i.e., N^+) would have resulted from the four bound moieties. A reading of the specification at page 26, line 28 to page 28, line 18, in view of former formula (7), clearly indicates to one skilled in the art that a quaternary amine was not contemplated because a counterion is not depicted or described. Therefore, amended formula (7) corrects the obvious error and comports with the original description.

Claims 29-53, 59 and 62 will be pending after entry of the amendment.

A. Non-Statutory Obviousness-Type Double Patenting Rejections

1. U.S. Patent No. 7,008,904

Claims 29-53 stand rejected on the ground of nonstatutory obviousness-type double patenting as not being patentably distinct over claims 1-10, 32, 37-39, 52, 53, 61, 89-92 and 107 of U.S. Patent No. 7,008,904.

The Office asserts (i) that the bipyridilium herbicide of US '904 claim 1 is a pyridine herbicidal derivative of instant 29, (ii) that the subject matter of the claims of US '904 and the instant claims overlap, and (iii) that the difference between the claims of US '904 and the instant claims resides in different concentrations and ratios of components used in the claimed compositions and that "it is routine optimization for one of ordinary skill in the art to adjust the amount of ingredients to optimize the desired results."

Applicants respectfully submit that the double patenting rejection is improper and must be withdrawn because the subject matter of the claims of US '904 and the instant claims is patentably distinct and does not overlap. Therefore, the instant claims are not

anticipated by, or are not obvious over, the US '904 claims. In particular, the bipyridilium herbicides of US '904 and the instantly claimed pyridine herbicidal derivatives belong to separate and distinct chemical genera. In support, attached are entries presented in the *Herbicide Handbook*¹ for the instantly claimed pyridine analog herbicides clopyralid, dithiopyr, picloram, thiazopyr and triclopyr and the bipyridilium herbicides diquat and paraquat as called for in US '904 claim 52. As indicated therein, clopyralid, clopyralid, dithiopyr, picloram, thiazopyr and triclopyr are identified as belonging to the pyridine genus and the respective chemical structures show that each is formed from (i.e., is an analog or a derivative of) a single pyridine molecule. Conversely, diquat and paraquat are identified as belonging to the bipyridilium herbicide genus. Examination of the diquat and paraquat structures indicates that they are, respectively, bi- and tri-cyclic quaternary ammonium compounds synthesized from the pyridine compounds 2,2'-bipyridine and 4,4'-bipyridine. For that reason, the bipyridiliums compounds diquat and paraquat are sometimes grouped in the genus of quaternary ammonium herbicides which is separate and distinct genus from pyridine herbicides (such as are instantly claimed).² The distinction between the instantly claimed pyridine analog herbicide genus and the bipyridilium herbicide genus of the US '904 claims is indicated in the present specification at page 39, line 14 to page 40, line 33, where diquat (page 39, line 19) and paraquat (page 40, line 2) are listed among many optional **one or more additional pesticides** that may be included in the claimed compositions; nowhere in the present specification are diquat or paraquat, or any other member of the bipyridilium herbicide genus, listed among the species of the pyridine herbicide genus (see generally specification pages 12-16).

Applicants therefore submit that the instant claims are patentably distinct from the US '904 claims and the instant claims are not anticipated by, or would not have been obvious over, the US '904 claims. Withdrawal of the nonstatutory obviousness-type

¹ See *Herbicide Handbook*, Weed Science Society of America, 8th ed. (2002) at pages 88-91 (clopyralid), pages 157-159 (dithiopyr), pages 345-348 (picloram), pages 419-420 (thiazopyr), pages 434-436 (triclopyr), pages 155-157 (diquat) and pages 333-335 (paraquat).

² See that attached herbicide classification taken from the online reference, *Compendium of Pesticide Common Names* that can be found at <http://www.alanwood.net/pesticides/> (accessed on 28 August 2008). The instantly claimed herbicides are among those listed in the pyridine herbicide genus on page 8 of 13 and the bipyridilium herbicides of US '904 (aka quaternary ammonium herbicides) are among those listed in the quaternary ammonium herbicide genus on pages 8-9 of 13.

double patenting of claims 29-53 over claims 1-10, 32, 37-39, 52, 53, 61, 89-92 and 107 of U.S. Patent No. 7,008,904 is therefore respectfully requested.

2. U.S. Patent Application Numbers 11/368,872, 11/227,577 and 11/438,573

Claims 29-53 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being not patentably distinct over claims 1-4, 7-10, 12-24, 26-38, 48, 63, 69-73 and 75-84 of copending U.S. Patent App. No. 11/368,873. Applicants thank Examiner Brown for the clarification provided to the undersigned attorney on 28 August 2008 in a telephone interview where it was noted that application number 11/368,873 should have instead been cited as 11/368,872.

Claims 29-53 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being not patentably distinct over claims 1, 9-11 and 15-17 of copending U.S. Patent App. No. 11/227,577.

Claims 29-53 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being not patentably distinct over claims 1, 11, 13, 15 and 16 of copending U.S. Patent App. No. 11/438,573.

Applicants note these provisional obviousness-type double patenting rejections over co-pending applications 11/368,862, 11/227,577 and 11/438,573 and will address the same at such time when the present application is indicated to contain allowable subject matter.

B. Rejection Under 35 USC §112, Second Paragraph

Claims 59, 33, 37-39 and 42 stand rejected under USC §112, second paragraph. Applicants presume that the Office intended to instead refer to "claims ~~29~~ 59, 33, 37-39 and 42" because claim 29 is an independent composition claim while claim 59 is a method claim that incorporates composition claim features. The Office asserts that the terms "derivatives" and "analogs" are not defined in the specification.

Applicants respectfully submit that claims 29, 33, 37-39 and 42 meet the requirements under USC §112, second paragraph, because the terms "derivatives" and "analogs" are defined in the specification with the requisite degree of clarity such that one skilled in the art is readily enabled to determine the scope of the claims.

Pyridine analogs are defined at page 13, lines 18-29 as a class (i.e., genus) of herbicides that includes the species triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr and picloram. As is evident from the attached entries from the *Herbicide Handbook*, each of those pyridine analog species is based on pyridine and differ by the identity of the substituted functional groups. Based on the specification and common general knowledge, it is submitted that it would be clear to one skilled in the art that pyridine analog herbicides are substituted pyridines.

Glyphosate derivatives are defined at page 12, lines 15-21 of the specification as "a salt, adduct, or a compound which is converted to glyphosate in plant tissues or which otherwise provides glyphosate ion." Derivatives of pyridine analogs are similarly defined at page 13, lines 30-34 as various forms of pyridine analog herbicides including salts and esters. Therefore a pyridine analog derivative, such as, for instance, picloram isooctyl ester or picloram triisopropanolamine salt (see *Herbicide Handbook* attachment at page 345) would yield the pyridine analog herbicide (e.g., picloram) as a derivation product.

The above explanation for glyphosate derivatives, pyridine analog herbicides, and pyridine analog derivatives comports with the definition provided by the Office at page 6 of the 23 June 2008 Office action.

Therefore, one skilled in the art is readily enabled to determine the scope of the claims based on the specification, and claims 29, 33, 37-39 and 42 meet the requirements under USC §112, second paragraph.

C. Rejection Under 35 USC §103

Claims 29-53, 59 and 62 are rejected under 35 USC §103(a) as being obvious over **Brigance** (US 2002/0155953 A1) and **Jimoh** (US 2003/0004063 A1).

1. The present invention

Glyphosate is very effective in killing or controlling the growth of unwanted plants. However, glyphosate uptake (i.e., absorption) by the plant and translocation through the plant is relatively slow. Thus, visual symptoms that a plant has been treated with glyphosate may not appear until one week or more after application to the plant. See the specification at page 1, lines 14-25.

The problem solution of the present invention is directed to combining a pyridine analog herbicide (or a herbicidal derivative thereof) with glyphosate (or a herbicidal derivative thereof), glyphosate being in excess, in the presence of a surfactant in order to achieve one of the objects of the present invention of obtaining both early symptoms of plant treatment that are associated with the pyridine analog herbicide and prolonged control of the plant associated with glyphosate (see the specification at page 1, lines 6-13, and page 12, lines 2-8). Early symptoms of plant treatment are visible in 4 days or less after treatment (see the specification at page 19, lines 5-9). Problematically, the prior art teaches that pyridine analog herbicides can be antagonistic (i.e. can reduce) the herbicidal activity of glyphosate or a herbicidal derivative thereof (see the specification at page 19, lines 10-12). In accordance with the present invention, it has been discovered that combining glyphosate in a weight percent a.e. excess over the pyridine analog herbicide solves the antagonism problem and provides enhanced early symptoms of herbicidal efficacy for the combination of herbicides as compared to what would be expected from the additive effect of the herbicides individually applied. The present invention therefore allows for early plant kill, increased herbicidal efficacy and lower herbicide application rates for the claimed combination as compared to the herbicides applied individually. Lower herbicide application rates result in cost savings and less unwanted environmental exposure.

Applicants have discovered that the claimed co-herbicide combination provides enhanced early symptoms of herbicidal efficacy. See, for instance, Table 4.4.1 at pages 69-70 of the specification, where the claimed co-herbicide combination was shown to provide enhanced early symptoms of herbicidal efficacy on Fescue/Blue and Golden Rod at 5 DAT as compared to what would be expected from the additive effect of the herbicides individually applied. Under the Colby method for estimating synergy³, an

³ See Colby, S.R., "Calculating synergistic and antagonistic response of herbicide combinations," Weeds, 15, 20-22, 1967 (attached). The Colby method is widely accepted by those skilled in the art as a method for determining whether herbicide combinations show antagonism or synergy. Under the Colby method, the expected efficacy for a herbicide combination is calculated from the efficacy of those herbicides applied individually according to the equation:

$$E = X + Y - XY/100$$

where E is the expected herbicidal efficacy, X is the percent inhibition of growth by herbicide A (i.e., glyphosate) and Y is the percent inhibition of growth by herbicide B (i.e., triclopyr). For Fesc/Blue from

expected herbicidal efficacy for the combination of glyphosate (Roundup Brush) and triclopyr (Brush-B-Gone) when applied to Fesc/Blue is 75 and when applied to Golden Rod is 70. For Fesc/Blue, the actual efficacy at 5 DAT for the compositions containing glyphosate and triclopyr in the ratio range of 6:1 (i.e., 18+3 as reported in Table 4.1.1) to 36:1 (i.e., 18+0.5) exceeded the expected value of 75 thereby indicating enhanced efficacy for the claimed compositions. For Golden Rod, the actual efficacy at 5 DAT for the compositions containing glyphosate and triclopyr in the ratio range of 6:1 (i.e., 18+3) to 9:1 (i.e., 18+2) exceeded the expected value of 70 thereby indicating enhanced efficacy at 5 DAT for the claimed compositions.

2. The legal standard for establishing a *prima facie* case of obviousness

The Supreme Court decision in *KSR International Co. v. Teleflex Inc.*, 82 USPQ2d 1385 (2007) clarified the guidelines for making a proper determination of obviousness under 35 U.S.C. §103. The *KSR* Court rejected a rigid application of the teaching, suggestion or motivation test in an obviousness inquiry and held that there must be a reason for one skilled in the art to modify and/or combine the elements of the prior art in a particular manner that would yield the claimed invention.⁴

In response to *KSR*, the USPTO issued new guidelines for examiners regarding the obviousness standard (72 Fed. Reg. 57526-35, 10/10/07) and revised MPEP §2141 to articulate rationales to support rejections under 35 USC §103 as follows: (A) Combining

table 4.4.1 of the instant application, an expected efficacy (E) of 75 is calculated from the individual efficacies as follows: $(50 + 50) - (50)(50)/100 = 75$. For Goldenrod from table 4.4.1, (E) of 70 is calculated from the individual efficacies as follows: $(50 + 40) - (50)(40)/100 = 70$.

⁴ ...a patent composed of several elements is not proved obvious merely by demonstrating that each of its elements was, independently, known in the prior art. Although common sense directs one to look with care at a patent application that claims as innovation the combination of two known devices according to their established functions, *it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does*. This is because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known. (Emphasis added.) *KSR*, 82 USPQ2d at 1396.

Often, it will be necessary ... to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue. To facilitate this review, this analysis should be made explicit. *KSR*, 82 USPQ2d at 1396.

prior art elements according to known methods to yield **predictable results**; (B) Simple substitution of one known element for another to obtain **predictable results**; (C) Use of known technique to improve similar devices (methods or products) in the same way; (D) Applying a known technique to a known device (method or product) ready for improvement to yield **predictable results**; (E) "**Obvious to try**" - choosing from a finite number of identified, **predictable solutions, with a reasonable expectation of success**; (F) Known work in one field of endeavor may prompt variations of it for use in either the same field or a different one based on design incentives or other market forces if the variations are **predictable** to one of ordinary skill in the art; and (G) Some **teaching, suggestion or motivation** in the prior art that would have led one of ordinary skill to modify the prior art reference teachings to arrive at the claimed invention (emphasis added). In view of the above, the guidelines supporting an obviousness rejection under 35 USC §103 may be summarized into three basic concepts (1) predictable results; (2) obvious to try; and (3) teaching, suggestion, or motivation to combine references.

In view of the MPEP and the *KSR* case, it is clear that, to establish a *prima facie* case of obviousness, the Office must (1) show that each claimed element is described in the prior art; (2) show a reason to combine the prior art elements to produce the claimed invention; and (3) show a reasonable expectation of success and at least some degree of predictability.

3. **Brigance**

Brigance is directed to adjuvant compositions for pesticide formulations having reduced eye irritancy and comprising a mixture of a polyoxyalkylene aliphatic amine, a mixture of polyhydric alcohols and a metal-complexing carboxylic acid. Disclosed at paragraph [0018] are 17 exemplary herbicides including glyphosate and picloram. From the list of 17 herbicides, 136 two herbicide compositions are possible.⁵ Of those herbicides, only glyphosate is described as preferred; no preference for picloram or a mixture of picloram and glyphosate is described or suggested. Each example is directed to glyphosate; no mixed herbicide examples are presented.

⁵ Calculated as number of combinations = total number of permutations/number of permutations of each set. Mathematically: ${}^nC_r = n!/r!(n-r)! = 17!16/2!1! = 272/2 = 136$ possible combinations of two herbicide compositions from a set of 17 herbicides.

Brigance provides no teaching, suggestion or motivation to one skilled in the art to select the specific combination of glyphosate and picloram from the 136 possible co-herbicide combinations. Nor does **Brigance** teach or suggest that glyphosate-pyridine analog herbicide antagonism can be overcome by formulating glyphosate in excess, or that herbicidal efficacy for the claimed combination is greater than what would be expected based on the herbicidal efficacy of the herbicides applied individually.

4. **Jimoh**

Jimoh is directed to liquid concentrate herbicidal emulsion compositions comprising a water soluble herbicide and an oil soluble herbicide selected from a 192 member Markush group that includes the pyridine analog herbicides dithiopyr and thiazopyr (see claims 1, 28, 55, 85 and 112 and paragraph [0031]). Glyphosate and the pyridine analog herbicides clopyralid and triclopyr are among the 52 water-soluble herbicides that are described and claimed (see claims 6, 33, 59, 89 and 116 and paragraph [0027]). Among the water soluble herbicides, bialaphos, glufosinate, glyphosate and the imidazolinone herbicides imazamethabenz, imazamox, imazapic, imazapyr, imazaquin and imazethapyr are described as preferred. Among the water insoluble herbicides, a total of 191 are described as preferred (see paragraph [0032]). From the list of 9 preferred water soluble herbicides and 191 preferred water insoluble herbicides, 1719 possible herbicide combinations are calculated.⁶ **Jimoh** provides no teaching, suggestion or motivation to one skilled in the art to select the specific combination of glyphosate-dithiopyr or glyphosate-thiazopyr from the 1719 possible glyphosate-pyridine analog co-herbicide combinations.

From among the 52 disclosed water soluble herbicides disclosed by **Jimoh**, combinations of glyphosate and the pyridine analog herbicides clopyralid or triclopyr are but two out of a possible 1326 two water soluble herbicide combinations. Further, **Jimoh** teaches that those water soluble herbicides must be combined with a water insoluble herbicide selected from 191 total herbicides that includes the pyridine analog herbicides dithiopyr and thiazopyr. Therefore to arrive at the glyphosate-pyridine analog compositions of the present invention, one skilled in the art would have to select the

⁶ Calculated as number of combinations $9 \times 191 = 1719$ possible combinations of preferred water soluble herbicides and water-insoluble herbicides.

combination of the water soluble herbicides glyphosate and clopyralid or glyphosate and triclopyr and further combine that selection with dithiopyr or thiazopyr specifically selected from among the 191 possible preferred water insoluble herbicides. Nor does **Jimoh** teach or suggest that glyphosate-pyridine analog herbicide antagonism can be overcome by formulating glyphosate in excess, or that herbicidal efficacy for the claimed combination is greater than what would be expected based on the herbicidal efficacy of the herbicides applied individually.

5. The Office has failed to establish a *prima facie* case of obviousness over the cited art

In view of the above, Applicants respectfully submit therefore that the Office has failed to establish a prima facie case of obviousness of claims 29-53, 59 and 62 under 35 USC §103(a) over **Jimoh** and **Brigance**. Applicants concede that the Office showed that each claimed element is described in the prior art. However, the Office failed to show any reason that would direct one skilled in the art to select and combine the prior art elements from among the multitude of possible combinations disclosed in those references in order to arrive at the instant claims with any expectation of success. A close reading of the cited references clearly indicates that the combination of claimed elements would not have been apparent to one skilled in the art without Applicants' disclosure as a blueprint (which the Office had the benefit of utilizing).⁷ It is respectfully submitted therefore that one skilled in the art would not have been motivated to combine **Brigance** and **Jimoh** to arrive at the problem solution of the present claims with any expectation of success. The Office cannot properly maintain such an "obvious to try" rejection where there are so many potential solutions and where the results of such combinations are unpredictable.

⁷ M.P.E.P. §2142 further provides that in order to reach a proper determination under 35 U.S.C. §103(a), the Examiner must step backward in time and into the shoes worn by the hypothetical "person of ordinary skill in the art" when the invention was unknown and just before it was made. Knowledge of Applicants' disclosure must be put aside in reaching this determination, yet kept in mind in order to determine the "differences." The tendency to resort to "hindsight" based upon Applicants' disclosure is often difficult to avoid due to the very nature of the examination process. However, as stated by the Federal Circuit, impermissible hindsight must be avoided and the legal conclusion must be reached on the basis of the facts gleaned from the prior art. *Grain Processing Corp. v. American-Maize-Products, Co.*, 840 F.2d 902, 904 (Fed. Cir. 1988).

Even if it could somehow be said that one skilled in the art would have made such a selection, nowhere do **Brigance** or **Jimoh**, alone or in combination, teach or suggest that objects of the present invention including (i) overcoming glyphosate-pyridine analog herbicide antagonism by formulating glyphosate in excess or (ii) realizing herbicidal efficacy for the claimed combination that is greater than what would be expected based on the herbicidal efficacy of the herbicides applied individually could be realized by the instantly claimed combination. In view of those references, the results achieved by the present invention are unexpected, and claims 29-53, 59 and 62 are nonobvious under 35 USC §103(a) over **Jimoh** and **Brigance** for this additional reason.

D. Conclusion

Therefore, Applicants respectfully submit that claims 29, 33, 37-39 and 42 meet the requirements under USC §112, second paragraph and claims 29-53, 59 and 62 are nonobvious under 35 USC §103(a) over **Jimoh** and **Brigance**. Withdrawal of the rejection and allowance of the claims is respectfully requested.

The Commissioner is hereby authorized to charge any underpayment and credit any overpayment of government fees to Deposit Account No. 19-1345.

Respectfully submitted,



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HERBICIDE HANDBOOK

Eighth Edition

2002

Editor: William K. Vencill

Herbicide Handbook Committee¹:

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¹See page vii for affiliations.

Use classification: All products are General Use.

Synthesis and Analytical Methods

Synthesis: React *N*-(2-chlorophenylmethyl)hydroxylamine with chloropivaloyl chloride, followed by ring closure with methanolic KOH.

Purification of technical: Recrystallization from organic solvents, or distillation.

Analytical methods: Reverse phase HPLC under temperature control is used for analysis of technical and formulated products. GC may be used for analysis of formulated products and is used with N-P detection or GC-MS detection for analysis of residues.

Historical: Clomazone was developed in the early 1980s and commercialized as COMMAND in 1985. It is protected under U.S. patent 4,405,357. Numerous foreign patents also have been assigned.

Information Sources

Primary information source: FMC.

References

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7. Weimer, M. R. et al. 1992. *Pestic. Biochem. Physiol.* 42:43.
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9. Ferhatoglu, Y., M. Barrett, and J. Chappell. 2002. Abstracts WSSA 42:73.

CLOPYRALID

3,6-dichloro-2-pyridinecarboxylic acid

Nomenclature

Common name: clopyralid (ANSI, BSI; WSSA).

Manufacturers, products, and formulations

Dow AgroSciences: RECLAIM™, STINGER™, LONTREL® Turf and Ornamental and TRANSLINE™, 360 g ae/L (3 lb ae/gal), monoethanolamine (mea) salt, SL; CONFRONT™, mix of triclopyr + clopyralid at 270

+ 90 g ae/L (2.25 + 0.75 lb ae/gal), triethylamine salts, SL; CURTAIL™, mix of clopyralid + 2,4-D at 45.6 + 240 g ae/L (0.38 + 2 lb ae/gal), monoethanolamine and triisopropylamine salts, SL; HORNET WDG, mix of flumetsulam (18.5% ai) + clopyralid potassium salt (60.0% ai); REDEEM Rand P, mix of triclopyr + clopyralid 270 + 90 g ae/L, triethylamine salt, SL; CURTAIL M, mix of clopyralid + MCPA 50 + 282 g ae/L, 2-ethylexyl ester, EC.

Dupont: ACCENT-GOLD®, a mix of clopyralid +

flumetsulam + nicosulfuron + rimsulfuron at 51.7 + 19.1 + 6.5 + 6.5%, DG.

Other names: CAMPAIGN; CRUSADER; 3,6-DCP; DOWCO 290; ESCORT; HARRIER; LONTREL; MAYCLEN; VULCAN; Acid dichloro-3,6 picolinique (France); 3,6-dichloropicolinic acid (Canada and Finland); 3,6-dichloropyridine-2-carboxylic acid.

Chemical family: Pyridinecarboxylic acid or picolinic acid.

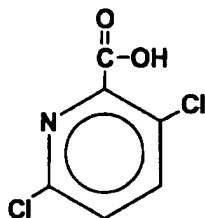
AWLN: Acid (6N) bVQ cG fG; Mea salt (6N) bVQ cG fG & Z2Q; Tea salt (6N) bVQ cG dZ eG fG & 2J2&2.

CAS number: Acid 1702-17-6; Mea salt 57754-85-5.

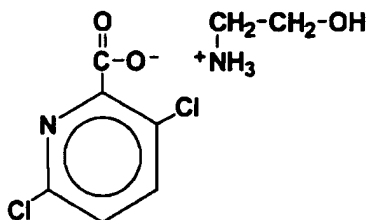
Chemical and Physical Properties

Chemical structure

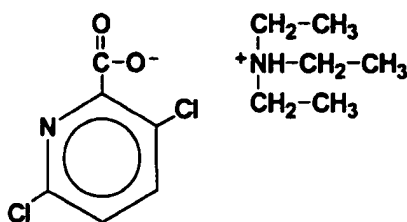
Clopyralid acid



Clopyralid monoethanolamine salt



Clopyralid triethylamine salt



Molecular formula: Acid $C_6H_3Cl_2NO_2$; Monoethanolamine (Mea) salt $C_8H_{10}Cl_2N_2O_3$; Triethylamine (Tea) salt $C_{12}H_{18}Cl_2N_2O_2$.

Molecular weight: Acid 192.00; Mea salt 253.09; Tea salt 293.19.

Description: Off-white crystalline solid, odorless.

Density: 0.298 g/mL (18.5 lb cu. Ft)

Melting point: 151-152°C

Boiling point: Not applicable.

Vapor pressure: 1.36 mPa at 25°C

Stability: Unstable in acid, oxidizing material, and halogenated organics; Stable to UV light; Decomposes above 151°C.

Solubility

Acid

water 1000 mg/L at 25°C

organic solvents g/100 mL at 25°C:

octanol 13.9

hexane 0.50

xylene 0.65

Monoethanolamine salt

water 300,000 mg/L at 25°C (ref. 7)

pK_a: 2.3

K_{ow}: -1.81 at pH 5, -2.63 at pH 7, and -2.55 at pH 9.

Herbicidal Use

Clopyralid can be applied POST at 0.105-0.28 kg ae/ha (0.094-0.25 lb ae/A) in sugarbeets, Christmas trees (conifers), grasses for seed, fallow, and field corn, and POST at 0.14-0.56 kg ae/ha (0.125-0.5 lb ae/A) in pasture, rangeland, and on Conservation Reserve land. It controls many annual and perennial broadleaf weeds including Canada thistle, wild buckwheat, cocklebur, jimsonweed, ragweed spp., marshelder, and wild sunflower.

Use Precautions

Fire hazard: STINGER, TRANSLINE, and RECLAIM are combustible; flash point is 47°C (117°F). CONFRONT is combustible; flash point is 66°C (150°F). CURTAIL is non-combustible; flash point is >91°C (>195°F).

Corrosiveness: STINGER, TRANSLINE, RECLAIM, and CONFRONT corrode brass, copper, zinc, and aluminum. CURTAIL corrodes brass and copper.

Storage stability: Stable for 2 yr. Store CONFRONT, RECLAIM, STINGER, and TRANSLINE above -2.2°C (28°F) or warm to 4.4°C (40°F) and agitate before use. Store CURTAIL above -12°C (10°F) or warm and agitate before use.

Cleaning glassware/spray equipment: Rinse and flush equipment at least three times with water; add household ammonia at 1% v/v during the second rinse.

Emergency exposure: Wash skin with soap and water. Wash eyes with water or injury may result. If CONFRONT is ingested, drink a large quantity of milk, egg whites, or gelatin solution, or, if these are not available, water. For other formulated products, induce vomiting if large amounts are ingested.

Incompatibilities: All formulated products are compatible with most types of hard water.

Behavior in Plants

Symptomology: Symptoms are typical of other auxin-type herbicides, and include epinastic bending and twisting of stems and petioles, stem swelling (particularly at nodes) and elongation, and leaf cupping and curling. This is followed by chlorosis at the growing points, growth inhibition, wilting, and necrosis. At low concentrations, the tips of young leaves may develop narrow feather-like extensions of the midrib.

Absorption: Readily absorbed by roots and foliage. In sunflower and rapeseed, 97% of foliar-applied clopyralid was absorbed within 24 h of application (2). Clopyralid parent acid is more rapidly absorbed than either the ester or salt forms. Under conditions of low humidity or water stress, absorption of the monoethanolamine and K salts are greatly reduced, whereas the acid and ester forms are unaffected. Uptake of clopyralid across plant membranes occurs by diffusion of the parent acid, and presumably leads to accumulation of clopyralid in cells due to ion trapping that is common with most weak acid herbicides.

Translocation: Readily transported in plant tissues, primarily via the symplasm (including the phloem). Over 50% of applied clopyralid translocated out of the treated leaves of Canada thistle within 24 h of application (3). Clopyralid accumulates at the growing points. Salt forms of clopyralid translocate less than the parent acid, but twice as much as the esters (1). This appears to result from increased partitioning of clopyralid esters in the cuticle.

Mechanism of action: Not completely understood but similar to that of endogenous auxin (IAA) and other auxin-type herbicides. The specific cellular or molecular binding site relevant to the action of IAA and the auxin-type herbicides has not been identified. Nevertheless, the primary action of these compounds appears to involve cell wall plasticity and nucleic acid metabolism. Clopyralid is thought to acidify the cell wall by stimulating the activity of a membrane-bound ATPase proton pump. The reduction in apoplastic pH induces cell elongation by increasing the activity of enzymes responsible for cell wall loosening. Low concentrations of clopyralid also stimulate RNA polymerase, resulting in subsequent increases in RNA, DNA, and protein biosynthesis. Abnormal increases in these processes presumably lead to uncontrolled cell division and growth, which results in vascular tissue destruction. In contrast, high concentrations of clopyralid and other auxin-type herbicides inhibit cell division and growth, usually in meristematic regions that accumulate photosynthate assimilates and herbicide from the phloem. Clopyralid and other auxin-type herbicides stimulate ethylene evolution which may in some cases produce the characteristic epinastic symptoms associated with exposure to these herbicides (5).

HRAC/ WSSA Group Designation: HRAC - O/ WSSA - 4.

Metabolism in plants: Slowly metabolized in most plants. In Canada thistle, no clopyralid metabolites were found 9 d after treatment in one study, whereas 22% of the herbicide

was present as water-soluble metabolites 6 d after application in another study (2, 6). Rapeseed rapidly metabolized clopyralid, with 38 and 70% converted to water-soluble metabolites 1 and 6 d after treatment, respectively (6).

Non-herbicidal biological properties: None known.

Mechanism of resistance in weeds: No known cases of resistance.

Behavior in Soil

Sorption: Weakly adsorbed. Clopyralid is dissociated and negatively charged in soil because of its low pK_a .

K_{oc} : Average is 6 mL/g (7), but ranges to 60 mL/g (increased soil sorption with time).

K_d : 0.41

Transformation

Photodegradation: Negligible losses.

Other degradation: Degraded by microbes. Non-microbial degradation does not occur.

Persistence: Moderate residual with an average field half-life of 40 d (7). Half-life was 12-70 d across a range of U.S. soils. Residues may injure certain crops (such as peas, lentils, and potatoes) planted 1 yr after application.

Mobility: Moderate leaching potential.

Volatilization: Insignificant losses.

Toxicological Properties

Toxicity tests were conducted with technical grade clopyralid acid unless otherwise indicated.

Acute toxicity

Clopyralid acid technical: Oral LD_{50} rat, mouse >5000 mg/kg; Dermal LD_{50} rabbit >2000 mg/kg; 4-h Inhal. LC_{50} rat >1.3 mg/L; Skin irrit. rabbit, none or very slight; Skin sensitiz. guinea pig, no; Eye irrit. rabbit, severe (possible corneal injury and permanent vision impairment).

STINGER: Oral LD_{50} rat >5000 mg/kg.

Subchronic toxicity

90-d dietary, mouse: NOEL 750 mg/kg/d.

90-d dietary, rat: NOEL 300 mg/kg/d.

90-d dietary, dog: NOEL 150 mg/kg/d.

Chronic toxicity

18-mo dietary, mouse: NOEL 500 mg/kg/d; not oncogenic.

24-mo dietary, rat: NOEL 50 mg/kg/d; not oncogenic.

12-mo dietary, dog: NOEL 100 mg/kg/d.

Teratogenicity

Rat: NOEL >250 mg/kg/d; not teratogenic.

Rabbit: NOEL 110 mg/kg/d; not teratogenic.

Reproduction

Rat: NOEL 500 mg/kg/d; not a reproductive toxin.

Mutagenicity

Gene mutation: Ames test, negative; CHO/HGPRT, negative.

Structural chromosome aberration: Mouse bone marrow, negative.

DNA damage/repair: Rat UDS, negative.

Wildlife

Clopyralid acid technical: Bobwhite quail 8-d dietary LC_{50} >4640 ppm; Mallard duck, oral LD_{50} 1465 mg/kg, 8-d dietary LC_{50} >4640 ppm; Earthworm LC_{50} in soil 1000 ppm; Honey bee, oral LD_{50} 100 µg/bee, topical LD_{50} >0.1 µg/bee; Daphnia 48-h LC_{50} 232 mg/L; Bluegill sunfish 96-h LC_{50} 125 mg/L; Rainbow trout 96-h LC_{50} 104 mg/L.

Use classification: General Use for all products.

Synthesis and Analytical Methods

Synthesis: Not available.

Purification of technical: Not available.

Analytical methods: See ref. 4.

Historical: Clopyralid was discovered in 1961. The original patent has expired. Clopyralid was first marketed in 1978 in Europe. In the U.S., CURTAIL was introduced in 1987, STINGER in 1988, and CONFRONT in 1989.

Information Sources

Primary industry source: Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, IN 46268-1054.

References

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2. Hall and Vanden Born. 1988. Weed Sci. 36:9.
3. O'Sullivan and Kossatz. 1984. Weed Res. 24:17.
4. Pik and Hodgson. 1976. J. AOAC 59:2.
5. Thomson and Cobb. 1987. Proc. Br. Crop Prot. Conf.-Weeds 3:1097.
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7. Wauchope, R. D. et al. 1992. Rev. Environ. Contam. Toxicol. 123:1.

First used in 1955 as a growth regulator. British patent 785,732 was applied for in 1955.

Information Sources

Primary industry source: Syngenta.

References

1. Brian, R. C. 1967. *Ann. Appl. Biol.* 59:91.
2. Dodge, A. D. 1982. Pages 57-77 in D. E. Moreland, J. B. St. John, and F. D. Hess, eds., *Biochemical Responses Induced by Herbicides*. Am. Chem. Soc. Symp. Ser. No. 181, Washington, D.C.

3. Dodge, A. D. 1991. Pages 165-176 in J. C. Caseley, G. W. Cussans, and R. K. Atkin, eds., *Herbicide Resistance in Weeds and Crops*. Butterworth-Heinemann, Oxford.
4. Funderburk and Lawrence. 1964. *Weeds* 12:259.
5. Wauchope, R. D. et al. 1992. *Rev. Environ. Contam. Toxicol.* 123:1.
6. Zweig, G., ed. 1967. *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives*, Vol. 5. Academic Press, New York.

DITHIOPYR

S,S-dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarbothioate

Nomenclature

Common name: Dithiopyr (ANSI, ISO, WSSA).

Manufacturers, products, and formulations

Dow Agro: DIMENSION, 119.8 g ai/L (1 lb ai/gal), EC; DIMENSION 0.1G, 0.1% ai; DIMENSION 0.25G, 0.25% ai, GR; STAKEOUT 1G, 1% ai, GR.

Other names: MON 7200; MON 15100; MON 15151; RH-101664; 3,5-pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-*S,S*-dimethylester; *S,S'*-dimethyl-2-difluoromethyl-4-isobutyl-6-trifluoromethylpyridine-3,5-dicarbothioate.

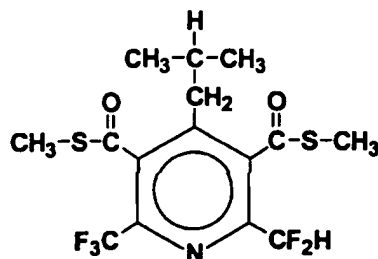
Chemical family: Pyridine.

AWLN: (6N) bYFF cVS1 d1Y1&l eVS1 fXFF

CAS number: 97886-45-8

Chemical and Physical Properties

Chemical structure



Molecular formula: $C_{15}H_{16}F_5NO_2S_2$

Molecular weight: 401.41

Description: Crystalline, colorless, faint odor.

Density: 1.42 g/mL at 20°C

Melting point: 65°C

Boiling point: 52°C at 760 mm Hg

Vapor pressure: 0.53 mPa (4×10^{-6} mm Hg) at 25°C

Stability: >2 yr at >0°C

Solubility: water 1.38 mg/L at 20°C

pK_a : None.

K_{ow} : 56,250

Herbicidal Use

Dithiopyr is applied PRE at 0.056-0.56 kg ai/ha (0.05-0.5 lb ai/A) or POST at 0.14-0.56 kg ai/ha (0.125-0.5 lb ai/A) in direct-seeded and transplanted rice; PRE at 0.14-0.56 kg ai/ha or POST at 0.56 kg ai/ha in established turf [maximum single application to turf is 0.56 kg ai/ha with total amount not to exceed 1.68 kg ai/ha (1.5 lb ai/A)]; and PRE at 0.14-2.24 kg ai/ha (0.125-2 lb ai/A) in ornamentals, trees, and other perennial crops. Dithiopyr controls several annual grass and small-seeded broadleaf weeds such as barnyardgrass, crabgrass spp., goosegrass, *Oxalis*, and spurge.

Use Precautions

Fire hazard: Technical and DIMENSION EC are nonflammable; flash points are 84°C (183°F) and 63°C (145°F), respectively.

Corrosiveness: Copper, iron, and zinc were not corroded after a 2-wk exposure to DIMENSION EC in sunlight at 52°C (126°F).

Storage stability: Technical and dithiopyr granules are stable. DIMENSION EC may crystallize below 0°C (32°F), but can be re-dissolved by shaking at temperatures >15°C (>59°F).

Cleaning glassware/spray equipment: Not available.

Emergency exposure: If ingested, do not induce vomiting. Drink large quantities of water and get medical attention. Dimension EC is severely irritating to eyes and skin.

Incompatibilities: None known.

Behavior in Plants

Symptomology: Dithiopyr inhibits mitosis causing swelling in meristematic regions such as root tips.

Absorption/Translocation: Absorbed by roots and to some degree by the foliage of susceptible plants. Most important site of uptake appears to be meristematic regions since dithiopyr translocation is limited and the primary site of action seems to be meristematic tissues.

Mechanism of action: Inhibits mitosis in late prometaphase. Dithiopyr does not bind to tubulin but to another protein that may be a microtubule associated protein (MAP). MAPs function in microtubule stability. Dithiopyr results in shortened microtubules that cannot form the spindle fibers normally responsible for separating chromosomes to the poles of the cell during mitosis. Cortical microtubules, which normally prevent isodiametric cell expansion, also are essentially absent resulting in club-shaped root tips (1).

HRAC/WSSA Group Designation: HRAC - K1/WSSA - 3.

Metabolism in plants: Not available.

Non-herbicidal biological properties: Not available.

Mechanism of resistance in weeds: No known cases of resistance.

Behavior in Soil

Sorption: Strongly adsorbed to soil. Sorption is somewhat reversible on low OM soils.

K_{oc} : Average is 1638 mL/g.

K_d : 7.89 for a Sarpy soil with 0.8% OM, 8% clay, and pH 8; 12.82 for a Dupon soil with 1% OM, 8% clay, and pH 7.5; 45.93 for a Sharkey soil with 3.2% OM, 59% clay, and pH 6.2.

K_f and $1/n$: K_f 6.95 and $1/n$ 0.93 for a Sarpy soil; K_f 7.91 and $1/n$ 0.83 for a Dupon soil; K_f 26.92 and $1/n$ 0.86 for a Sharkey soil.

Transformation

Photodegradation: Only 5% of dithiopyr was photolyzed to a monoacid after application at 1.12 kg ai/ha to soil and an exposure equivalent to 33.6 d of sunlight at 25°C from a xenon arc lamp producing 198 mW/m² from 300-750 nm. Half-life was 17.6 d for dithiopyr at 0.7 ppm in buffered water without phototensitizers at 25°C, and primary metabolites were the two monoacids and the diacid.

Other degradation: Dithiopyr is microbially hydrolyzed to the two monoacids and the diacid (each at <6% of applied), respectively as follows: 3-pyridinecarboxylic acid,

2-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)-; 3-pyridinecarboxylic acid, 6-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-2-(trifluoromethyl)-; and 3,5-pyridinedicarboxylic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-. Non-biological degradation is negligible. Bound residues are minimal with 4% of applied dithiopyr remaining in the soil after Soxhlet extraction.

Persistence: Somewhat short to moderate persistence.

Field experiments: Half-life was 17 d with a range of 3-49 d across 14 turf sites representing diverse climates, soil textures, and irrigation methods. Metabolites were dissipated almost completely within 1 yr.

Mobility: Leaching of dithiopyr and its acid metabolites did not exceed 61 cm (24 inches), and was often <23-30 cm (<9-12 inches) even in sandy soil with low OM content and 249 cm (98 inches) of irrigation. Dithiopyr and its metabolites were not detected at >10 ppb between 61 and 244 cm (96 inches). Groundwater Ubiquity Score (GUS) for dithiopyr is <1.0. Potential for movement in runoff water is unlikely due to low water solubility and strong adsorption to turfgrass and soil.

Volatilization: In a field study, volatilization rate declined from 2%/h immediately after application to 0.1%/h 3 d after application. Total losses were 6.2-18.7% of applied during the first 3 d after application and were 12-40% during the 30-d study.

Formulation effects: Half-life of emulsifiable concentrate, microencapsulated, and granule formulations averaged 17, 36, and 61 d, respectively. These different half-lives presumably reflect differing volatilization losses.

Toxicological Properties

Toxicity tests were conducted with technical grade dithiopyr unless otherwise indicated.

Acute toxicity

Dithiopyr technical: Oral LD₅₀ rat >5000 mg/kg; Dermal LD₅₀ rabbit >5000 mg/kg; 4-h Inhal. LC₅₀ rat >6 mg/L; Skin irrit. rabbit, none; Skin sensitiz. guinea pig, no; Eye irrit. rabbit, slight.

DIMENSION: Oral LD₅₀ rat >3600 mg/kg; Dermal LD₅₀ rabbit >5000 mg/kg; 4-h Inhal. LC₅₀ rat 11 mg/L; Skin irrit. rabbit, severe; Skin sensitiz. guinea pig, no; Eye irrit. rabbit, severe.

DIMENSION 0.25G: Oral LD₅₀ rat >5000 mg/kg; Dermal LD₅₀ rabbit >5000 mg/kg; Skin irrit. rabbit, none; Skin sensitiz. guinea pig, no; Eye irrit. rabbit, slight.

Subchronic toxicity

90-d dietary, rat: NOEL 10 ppm; low levels of liver toxicity at >100 ppm.

90-d dietary, dog: NOEL 1 mg/kg/d; liver toxicity at >10 mg/kg/d.

Chronic toxicity

18-mo dietary, mouse: NOEL 3 ppm; liver and adrenal gland weight increases at >30 ppm; increased splenic

hematopoiesis, adrenal changes, and evidence of cholestasis at 300 ppm; not carcinogenic.

24-mo dietary, rat: NOEL 10 ppm; liver and kidney weight increases at 300 ppm; not carcinogenic.

12-mo dietary, dog: NOEL 0.5 mg/kg/d; liver toxicity (slight to moderate intrahepatic cholestasis) and brown pigment deposition in kidneys at 24 mg/kg/d.

Teratogenicity

Rat and rabbit: NOEL 1000 mg/kg/d; toxicity in dams at 1000 mg/kg/d.

Reproduction

Rat: NOEL 25 ppm; decreased weight gain, liver and kidney weight increases, and histopathological evidence of liver, kidney, thyroid, and adrenal toxicity at 250 and 2500 ppm.

Mutagenicity

Gene mutation: Ames test, negative; CHO, negative.

Structural chromosome aberration: Lung cells, negative.

DNA damage/repair: Primary hepatocytes, negative.

Wildlife

Dithiopyr technical: Bobwhite quail, oral LD₅₀ >2250 mg/kg, 5-d dietary LC₅₀ >5620 ppm; Mallard duck 5-d dietary LC₅₀ >5620 ppm; Earthworm LC₅₀ in soil >1000 ppm; Honeybee topical 48-h LC₅₀ 81 µg/bee; Daphnia 48-h LC₅₀ >1.7 mg/L; Bluegill sunfish 96-h LC₅₀ 0.7 mg/L; Carp 96-h LC₅₀ 0.72 mg/L; Rainbow trout, 96-h LC₅₀ 0.48 mg/L.

Use classification: General Use for all products.

Synthesis and Analytical Methods

Synthesis: Not available.

Purification of technical: Not available.

Analytical methods: Not available.

Historical: First introduced by Monsanto Company, but purchased by Rohm and Haas in 1994. Dithiopyr is covered by U.S. patent 4,692,184.

Information Sources

Primary industry sources: Monsanto, and Rohm and Haas.

Reference

1. Vaughn and Lehnen. 1991. Weed Sci. 39:450.

DIURON

N'-(3,4-dichlorophenyl)-*N,N*-dimethylurea

Nomenclature

Common name: diuron (ANSI, BSI, ISO, WSSA).

Manufacturers, products, and formulations

AgriLiance LLC: DIURON 80DF, 80%, WG; DIURON 4L, 480 g ai/L, SC; TOTAL®, a mix of bromacil + diuron + sodium chlorate + sodium borate at 2 + 2 + 40 + 40% ai.

BASF: TOPSITE® 2.5G, mix of diuron + imazapyr isopropylamine salt at 2% ai + 0.5% ae, GR.

Drexel: DIURON 4L, 480 g ai/L (4 lb ai/gal), SC; DIURON 80W, 80% ai, WP; DIURON 80 HERBICIDE, 80% ai, WG.

Griffin: DIREX 4L®, 480 g ai/L, SC; DIREX 80DF, 80% ai, WG; Karmex, 50% ai, WG; Linex 4L, 480 g ai/L, SC; Linex 50DF, Lorox DF, 50% ai, WG.

Helena: WEED BLAST 4G, mix of diuron + bromacil at 2 + 2% ai, GR.

UAP-Platte: DIURON 80 WDG, 80% ai, WG; SURE-FIRE®, mix of paraquat dichloride salt + diuron at 240 g cation/L + 120 g ai/L (2 lb cation/gal + 1 lb ai/gal), SC;

PICLORAM

4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid

Nomenclature

Common name: picloram (ANSI, BSI, E-ISO, JMAF, WSSA).

Manufacturers, products, and formulations

Dow AgroSciences: GRAZON™ PC, TORDON™ K, and TORDON 22K, 240 g ae/L (2 lb ae/gal), K salt, SL; AC-CESST™, mix of triclopyr butoxyethyl ester + picloram isooctyl ester at 240 + 120 g ae/L (2 + 1 lb ae/gal), EC; GRAZON P+D and TORDON 101 MIXTURE, mix of picloram + 2,4-D at 65 + 240 g ae/L (0.54 + 2 lb ae/gal), triisopropanolamine (tipa) salts, SL; TORDON RTU and PATHWAY, mix of picloram + 2,4-D at 32.4 + 120 g ae/L (0.27 + 1 lb ae/gal), tipa salts, SL.

Other names: AMDON; BOROLIN; HYDON; K-PIN; piclorame (F-ISO); 4-amino-3,5,6-trichloropicolinic acid; 4-amino-3,5,6-trichloropyridine-2-carboxylic acid (IUPAC).

Chemical family: Pyridinecarboxylic acid or picolinic acid.

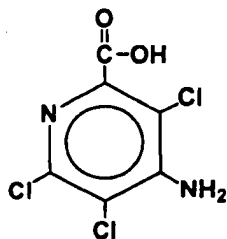
AWLN: Acid (6N) bVQ cG dZ eG fG; Isooctyl (2-ethylhexyl) ester (6N) bVOIY4&2 cG dZ eG fG; K salt (6N) bVO cG dZ eG fG .K; Tipa salt (6N) bVQ cG dZ eG fG &1Y1&JY1&1&Y1&1.

CAS number: Acid 1918-02-1; Isooctyl (2-ethylhexyl) ester 26952-20-5; K salt 2545-60-0; Tipa salt 6753-47-5.

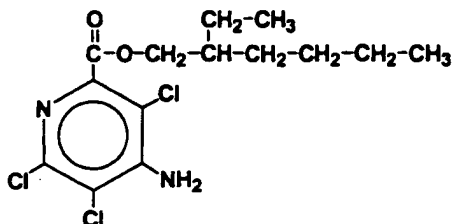
Chemical and Physical Properties

Chemical structure

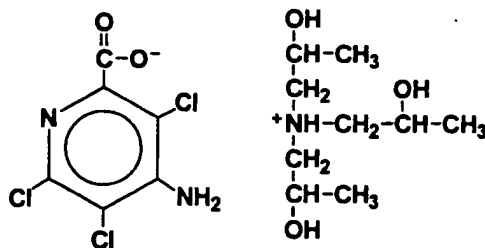
Picloram acid



Picloram isooctyl ester (2-ethylhexyl ester)



Picloram triisopropanolamine salt



Molecular formula: Acid $C_6H_3Cl_3N_2O_2$; Isooctyl ester (I ester) $C_{14}H_{19}Cl_3N_2O_2$; K salt $C_6H_2Cl_3KN_2O_2$; Triisopropanolamine (Tipa) salt $C_{15}H_{24}Cl_3N_3O_3$.

Molecular weight: Acid 241.46; I ester 353.68; K salt 279.55; Tipa salt 432.73.

Description: White powder, chlorine-like odor.

Density: Not available.

Melting point: Decomposes before melting.

Boiling point: Not applicable.

Vapor pressure: Acid 8.2×10^{-8} kPa (6.16×10^{-7} mm Hg) at 35°C, and 1.4×10^{-7} kPa (1.07×10^{-6} mm Hg) at 45°C.

Stability: Decomposed by UV light; Decomposes at ~215°C.

Solubility

Acid

water 430 mg/L at 25°C

organic solvents g/100 mL at 25°C:

acetone 1.98

ethanol 1.05

acetonitrile 0.16

isopropanol 0.55

benzene 0.02

kerosene 0.001

carbon disulfide <0.005

methylene chloride 0.06

diethyl ether 0.12

Potassium and triisopropylamine salts

water 200,000 mg/L at 25°C (estimated) (ref. 10)

pK_a : 2.3 at 22°C

K_{ow} : 1.4 at pH 7, 83.2 at pH 1

Herbicidal Use

Picloram can be applied as follows: foliar-applied at 0.14-1.12 kg ae/ha (0.125-1 lb ae/A) in forest plantings, noncrop areas such as rights-of-way and industrial sites, and wildlife openings in forests and noncrop areas; POST at 0.07-0.56 kg ae/ha (0.0625-0.5 lb ae/A) in pasture and rangeland; POST at 0.14-0.56 kg ae/ha on Conservation Reserve Program (CRP) land; POST at 18-27 g ae/ha (0.016-0.023 lb ae/A) in wheat, barley, and oats; POST at 0.14-0.28 kg ae/ha in fall-

low; cut surface (stump, tree injection, or girdle) treatments for woody species using undiluted PATHWAY or TORDON RTU; basal bark treatment as a 20-30% v/v solution of ACCESS in oil for control of trees <15 cm diam. Picloram controls certain annual broadleaf weeds at low rates and many annual and perennial broadleaf weeds, vines, and woody plants at higher rates. Grass weeds are not controlled. GRAZON PC and GRAZON P+D can be mixed with certain liquid fertilizers.

Use Precautions

Fire hazard: All products are nonflammable; flash points for TORDON 101 MIXTURE and GRAZON P+D are 46°C (115°F) (TCC), for PATHWAY and TORDON RTU are 41°C (106°F) (TCC), and for ACCESS is 68°C (154°F) (TCC). No flash point was observed for TORDON K, TORDON 22K, and GRAZON PC at up to 101°C (214°F) (TCC).

Corrosiveness: Slightly corrosive to mild steel after prolonged exposure at high temperatures. Noncorrosive to other metals.

Storage stability: If TORDON 101 and GRAZON P+D are exposed to subfreezing temperatures, they should be warmed to at least 4°C (39°F) and agitated before using. Store above -2°C (28°F) or warm and agitate before use.

Cleaning glassware/spray equipment: Rinse equipment three times with ammonia solution. Picloram residues are difficult to remove completely from spray equipment and low concentrations are phytotoxic to susceptible species. Thus, a sprayer used to apply picloram should not be used to spray foliage of susceptible plants.

Emergency exposure: Flush eyes with water for 15 min; consult a physician. Flush skin with water. If ACCESS is ingested, do not induce vomiting; consult a physician. For other formulated products, induce vomiting if large amounts are ingested; consult a physician. No specific antidote is available.

Incompatibilities: Not available.

Behavior in Plants

Symptomology: Symptoms of picloram injury are typical of other auxin-type herbicides, and include epinastic bending and twisting of stems and petioles, stem swelling (particularly at nodes) and elongation, and leaf cupping and curling. Leaf shape and venation often appear abnormal. This is followed by chlorosis at the growing points, growth inhibition, wilting, and necrosis. Death of susceptible plants occurs slowly, usually within 3-5 wk. At low concentrations, young leaves may appear puckered and the tips of new leaves may develop into narrow extensions of the midrib.

Absorption/translocation: Readily penetrates roots or foliage with foliar treatments, ester formulations are absorbed more quickly and in larger amounts than other formulations. In sunflowers and rapeseed, 97% of foliar-applied picloram was absorbed within 24 h of application (6). Picloram movement across the plasmalemma may involve both an active protein-mediated process and passive diffusion (1). Picloram is trans-

ported rapidly in plant tissues primarily via the symplastic pathway (including the phloem), eventually accumulating at the growing points (9). Over 60% of picloram absorbed by leaves of sunflowers and rapeseed moved out of the treated leaf within 6 d of application (6). Picloram also translocates significantly in the apoplasm (including the xylem) (8). Approximately 3% of foliar-applied picloram accumulated in roots of sunflowers and rapeseed (9) and in horsetail (5).

Mechanism of action: Not completely understood, but similar to that of endogenous auxin (IAA) and other auxin-type herbicides (2). The specific cellular or molecular binding site relevant to the action of IAA and the auxin-type herbicides has not been identified. Nevertheless, the primary action of these compounds appears to involve cell wall plasticity and nucleic acid metabolism. Picloram is thought to acidify the cell wall by stimulating the activity of a membrane-bound ATPase-driven proton pump. The reduction in apoplasmic pH induces cell elongation by increasing the activity of certain enzymes responsible for cell wall loosening. Low concentrations of picloram also stimulate RNA polymerase, resulting in subsequent increases in RNA, DNA, and protein biosynthesis. Abnormal increases in these processes presumably lead to uncontrolled cell division and growth, which results in vascular tissue destruction. In contrast, high concentrations of picloram and other auxin-type herbicides inhibit cell division and growth, usually in meristematic regions that accumulate photosynthate assimilates and herbicide from the phloem. These herbicides stimulate ethylene evolution which may in some cases produce the characteristic epinastic symptoms associated with exposure to these herbicides.

HRAC/WSSA Group Designation: HRAC - O/ WSSA - 4.

Metabolism in plants: Picloram metabolism appears to be slow in susceptible species, but more rapid in tolerant ones. Essentially no picloram metabolites were detected 16 d after treatment in horsetail (susceptible) (5), and only 17% of the picloram absorbed by leafy spurge (susceptible) was metabolized 4 d after application. Most metabolites are water-soluble and suspected to be sugar conjugates (6). Picloram conjugates with glucose in sunflowers to form an *N*-glucoside (3). Leafy spurge metabolized picloram to isomeric glucose esters, gentiobiose esters, and *N*-glucosides (4).

Non-herbicidal biological properties: None known.

Mechanism of resistance in weeds: Resistance has recently developed in a biotype of wild mustard from Canada and in yellow starthistle from Washington. The resistance mechanism is unknown, but may involve an altered auxin receptor site.

Behavior in Soil

Sorption: Weakly adsorbed to OM and certain clays, with somewhat greater adsorption to OM. Adsorption to soil increases as level of OM and clay increase.

K_{oc} : Average is 16 mL/g for the K salt (10), but ranges from 17-160 mL/g.

K_d : 0.5 mL/g

Transformation

Photodegradation: Rate of photodegradation is highest in clear, moving water and on soil and plant surfaces. Photolysis half-life in water is 2.6 d. Photolysis appears to involve cleavage of the pyridine ring.

Other degradation: Degraded somewhat slowly, primarily by aerobic microbial metabolism, resulting in CO₂ as an end-product metabolite. Subsequent degradation of primary degradation products is rapid, leaving only trace amounts of primary products.

Persistence: Average field half-life is 90 d (10), with a range of 20-300 d. Dissipation is more rapid under warm, humid conditions of the southeastern and south central U.S. than in the cool, dry conditions of the northern U.S. Picloram dissipates more rapidly in the presence of plant roots, with higher soil OM content, and at lower picloram concentrations.

Lab experiments: Half-lives were 23, 63, and 172 d for picloram at 2.5, 25, and 250 ppb, respectively, at 25°C with optimum moisture.

Mobility: Highly leachable in some situations, although most picloram residues are found in the top 61 cm (24 inches) of the soil profile. Leaching potential is greatest in sandy soils low in OM, and is affected by other soil and environmental factors as well as by application rate.

Volatilization: No losses.

Toxicological Properties

Toxicity tests were conducted with technical grade picloram acid unless otherwise indicated.

Acute toxicity

Picloram acid technical: Oral LD₅₀ male rat >5000 mg/kg, female rat 4012 mg/kg, mouse 2000-4000 mg/kg, rabbit ~2000 mg/kg, guinea pig ~3000 mg/kg, sheep >1000 mg/kg, cattle >750 mg/kg; Dermal LD₅₀ rabbit >2000 mg/kg; 4-h Inhal. LC₅₀ rat >0.035 mg/L; Skin irrit. rabbit, none; Skin sensitiz. guinea pig, no; Eye irrit. rabbit, moderate.

Picloram K salt technical: Oral LD₅₀ male rat >5000 mg/kg, female rat 3536 mg/kg; Dermal LD₅₀ rabbit >2000 mg/kg; 4-h Inhal. LC₅₀ rat >1.6 mg/L; Skin irrit. rabbit, none; Skin sensitiz. guinea pig, yes; Eye irrit. rabbit, moderate.

Picloram isooctyl ester (Io ester) technical: Oral LD₅₀ rat >3500 mg/kg; Dermal LD₅₀ rabbit >2000 mg/kg; 4-h Inhal. LC₅₀ rat >0.35 mg/L; Skin irrit. rabbit, mild; Eye irrit. rabbit, moderate, Skin sensitize, guinea pig.

Picloram triisopropanolamine (Tipa) salt technical: Oral LD₅₀ rat >5000 mg/kg; Dermal LD₅₀ rabbit >2000 mg/kg; 4-h Inhal. LC₅₀ rat >0.071 mg/L; Skin irrit. rabbit, slight; Skin sensitiz. guinea pig, yes; Eye irrit. rabbit, minimal.

Subchronic toxicity

90-d dietary, mouse: NOEL <1000 mg/kg/d for the technical acid and K salt; reversible liver effects.

90-d dietary, rat: NOEL 50 mg/kg/d for the technical acid

and K salt. NOEL 73 mg/kg/d for the technical Io ester; kidney and liver weight increase. NOEL 90 mg/kg/d for the technical Tipa salt.

90-d dietary, dog: NOEL 250 mg/kg/d for the technical acid and K salt; increased liver weight.

Chronic toxicity

24-mo dietary, mouse: Systemic NOEL 1000 mg/kg/d; not oncogenic.

24-mo dietary, rat: NOEL 20 mg/kg/d; not oncogenic.

12-mo dietary, dog: NOEL >175 mg/kg/d; not oncogenic.

Teratogenicity

Rat: NOEL >400 mg/kg/d for the technical acid and K salt; not teratogenic. NOEL 1000 mg/kg/d for the technical Io ester and Tipa salt; not teratogenic.

Rabbit: NOEL >400 mg/kg/d for the technical acid and K salt; not teratogenic. NOEL 500 mg/kg/d for the technical Io ester; not teratogenic. NOEL 1000 mg/kg/d for the technical Tipa salt; not teratogenic.

Reproduction

Rat: NOEL parental 200 mg/kg/d, reproductive 1000 mg/kg/d; not a reproductive toxin; renal effects.

Mutagenicity

Gene mutation: Ames test, negative for the technical acid, K salt, Io ester, and Tipa salt; CHO, negative for the technical Io ester and Tipa salt.

Structural chromosome aberration: *In vitro* cytogenetics, negative for the technical acid, K salt, and Io ester; Mouse micronucleus, negative for the technical Io ester and Tipa salt.

DNA damage/repair: UDS, negative.

Wildlife

Picloram acid technical: Bobwhite quail 8-d dietary LC₅₀ >5000 ppm; Japanese quail 8-d dietary LC₅₀ >5000 mg/kg; Mallard duck, oral LD₅₀ >2510 mg/kg, 8-d dietary LC₅₀ >5000 mg/kg; Pheasant 8-d dietary LC₅₀ >5000 mg/kg; Honey bee topical LD₅₀ >100 µg/bee; Daphnia 48-h LC₅₀ 34-76 mg/L; Bluegill sunfish 96-h LC₅₀ 14.5-44.5 mg/L; Fathead minnow 96-h LC₅₀ 55.3 mg/L; Rainbow trout 96-h LC₅₀ 5.5-19.3 mg/L.

Picloram K salt technical: Bobwhite quail 8-d dietary LC₅₀ >5620 ppm; Mallard duck oral LD₅₀ >2250 mg/kg; Honey bee topical LD₅₀ >63.8-226 µg/bee; Daphnia 48-h LC₅₀ >100 mg/L; Bluegill sunfish 96-h LC₅₀ 13-100 mg/L; Rainbow trout 96-h LC₅₀ 3.1-60 mg/L.

Picloram Io ester technical: Bobwhite quail 8-d dietary LC₅₀ >5620 ppm; Honey bee topical LD₅₀ >2250 µg/bee.

Picloram Tipa salt technical: Bobwhite quail 8-d dietary LC₅₀ >5000 ppm; Mallard duck oral LD₅₀ >2510 mg/kg; Honey bee topical LD₅₀ >100 µg/bee; Daphnia 48-h EC₅₀ 125 mg/L; Bluegill sunfish 96-h LC₅₀ 109 mg/L; Fathead minnow 96-h LC₅₀ 150 mg/L; Rainbow trout 96-h LC₅₀ 51 mg/L.

Use classification: PATHWAY and TORDON RTU are Gen-

eral Use. TORDON 24K, TORDON 22K, TORDON 101 MIXTURE, GRAZON P+D, and ACCESS are Restricted Use due to potential injury to susceptible non-target plants.

Synthesis and Analytical Methods

Synthesis: Not available.

Purification of technical: Not available.

Analytical methods: Product is analyzed using infrared at 10.04 μm . Residue analysis (chemical assay) for water samples with a test sensitivity of 0.1 ppb is available (ACR 68:14, Dow, September 26, 1968). Residue analysis for soil samples with a sensitivity of 5 ppb is available (ACR 73.3, Dow, May 21, 1973).

Historical: Picloram was discovered in 1960 and first reported in 1963 (7). Introduced by Dow Chemical Company as TORDON 101 in 1963, as TORDON 22K in 1964, as TORDON K in 1972, as TORDON RTU in 1979, and as ACCESS 1982. U.S. patent 3,285,925 was awarded to Dow in 1966.

Information Sources

Primary industry source: DowAgro Sciences LLC, 9330 Zionsville Road, Indianapolis, IN 462680-1054.

References

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2. Chang and Foy. 1983. *Pestic. Biochem. Physiol.* 19:203.
3. Chkanikov, D. I. et al. 1983. *Fiziol. Rast. (mosc)* 30(1):95.
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6. Hall and Vanden Born. 1988. *Weed Sci.* 36:9.
7. Laning, E. R. 1963. *Down to Earth.* 19:3.
8. O'Donovan and Vanden Born. 1981. *Can. J. Bot.* 59:1928.
9. Radosevich and Bayer. 1979. *Weed Sci.* 27:22.
10. Wauchope, R. D. et al. 1992. *Rev. Environ. Contam. Toxicol.* 123:1.
11. Woodburn, K.B. et al. 1989. *Environ. Toxicol. Chem.* 8:769.

THIAZOPYR

methyl 2-(difluoromethyl)-5-(4,5-dihydro-2-thiazolyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3-pyridinecarboxylate

Nomenclature

Common name: thiazopyr (ANSI, ISO, WSSA).

Manufacturers, products, and formulations

DowAgro Sciences: MANDATE 2EC, 240 g ai/L (2 lb ai/gal); VISOR 2E and SPINDLE 2E, 240 g ai/L (2 lb ai/gal), EC; Experimental formulations include a WG with 50% ai, and a GR with 5% ai.

Other names: MON 13200; RH-123652.

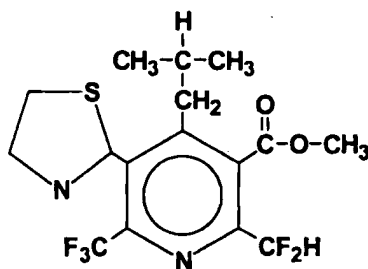
Chemical family: Pyridine.

AWLN: (6N) bYFF cVO1 d1Y1&1 fXFFF e- b(5NTSS)

CAS number: 117718-60-2

Chemical and Physical Properties

Chemical structure:



Molecular formula: C₁₆H₁₇F₅N₂O₂S

Molecular weight: 396.38

Description: Light tan crystalline solid, slight sulfur odor.

Density: 1.373 g/mL at 25°C

Melting point: 77.3-79.1°C

Boiling point: 236-282°C

Vapor pressure: 0.3 mPa (2 x 10⁻⁶ mm Hg) at 25°C

Stability: Not available.

Solubility

water 2.5 mg/L at 20°C

organic solvents g/100 mL at 20°C:

n-hexane 3.06

methanol 28.7

pK_a: None.

K_{ow}: 7729 at 21°C

Herbicidal Use

Thiazopyr can be soil-applied at 0.1-2.24 kg ai/ha (0.09-2 lb

ai/A) for control of grasses and certain small-seeded broad-leaf weeds. It has selectivity in several crops including alfalfa, cotton, peanuts, soybeans, tree crops, and vines. Limited testing has indicated its potential for use in sunflowers, sugarcane, transplanted vegetables, potatoes, small fruits and berries, and in forestry and industrial sites.

Use Precautions

Fire hazard: EC formulation is nonflammable; flash point is >93°C (>200°F).

Corrosiveness: Not available.

Storage stability: Shelf life of dry formulations is expected to be >2 yr under storage at <35°C (<95°F).

Cleaning glassware/spray equipment: Not available.

Emergency exposure: Wash skin with soap and water.

Incompatibilities: None known.

Behavior in Plants

Symptomology: Root growth inhibition and swelling in meristematic regions such as root tips. Susceptible plants may show thickened or swollen hypocotyls or internodes. Seed germination is not inhibited.

Absorption/translocation: Not available.

Mechanism of action: Disrupts cell division by inhibiting mitosis in late prometaphase and causing multipolar mitosis (2). Thiazopyr does not bind to tubulin but to a 65-68 kDa protein that may be a microtubule-associated protein (MAP). MAPs function in stabilization of growing microtubules. Thiazopyr shortens microtubules such that they cannot form the spindle fibers normally responsible for separating chromosomes to the poles of the cell during mitosis. Branched or multiple phragmoplasts are found in the zone of cell division. Cortical microtubules, which normally prevent isodiametric cell expansion, also are essentially absent, resulting in club-shaped root tips (1).

HRAC/ WSSA Group Designation: HRAC- K1/WSSA - 3.

Metabolism in plants: Thiazopyr is extensively and rapidly degraded to a large number of polar metabolites, each comprising <10% of the total applied thiazopyr residues. Major degradation reactions include sulfur oxidation, thiazoline ring opening and methyl ester hydrolysis, and transformation of the isobutyl side chain. The 2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethyl-3-pyridinecarboxylate moiety is found in most of the metabolites as well as in the parent thiazopyr.

Non-herbicidal biological properties: Not available.

Mechanism of resistance in weeds: Not available.

Behavior in Soil

Sorption: Not available.

Transformation

Photodegradation: Relatively rapid photolysis in water with a half-life of 15 d. Photodegradation on soil is insignificant.

Other degradation: Degraded primarily by microbes and secondarily by non-microbial hydrolysis. The monoacid degradation product was produced at low levels 20 d after application.

Persistence: Half-life averages 64 d, but ranges from 8-150 d. Dissipation rate varies with temperature, moisture, soil pH, and organic matter content. Wheat, grain sorghum, and sugarbeets are especially susceptible to soil residues of thiazopyr and may require rotational intervals.

Mobility: Low mobility. Thiazopyr has seldom been detected below 46 cm (18 inches) across numerous soils and agricultural regions in the U.S.

Volatilization: Insignificant losses.

Toxicological Properties

Toxicity tests were conducted with technical grade thiazopyr unless otherwise indicated.

Acute toxicity

Thiazopyr technical: Oral LD₅₀ rat >5000 mg/kg; Dermal LD₅₀ rabbit >5000 mg/kg; 4-h Inhal. LC₅₀ rat >1.2 mg/L; Skin irrit. rabbit, none; Skin sensitiz. guinea pig, no; Eye irrit. rabbit, slight.

Subchronic toxicity: Not available.

Chronic toxicity: Not available.

Teratogenicity

Rat and rabbit: NOEL NAV; not teratogenic.

Reproduction

Rat: NOEL NAV; not a reproductive toxin.

Mutagenicity: No evidence of mutagenicity or genotoxicity in several tests.

Wildlife

Thiazopyr technical: Bobwhite quail, oral LD₅₀ 1913 mg/kg, 8-d dietary LC₅₀ >5620 ppm; Mallard duck 5-d dietary LC₅₀ >5620 ppm; Honey bee, oral LC₅₀ >1000 ppm, topical LD₅₀ >100 µg/bee; Daphnia 48-h LC₅₀ 5.9 mg/L; Bluegill sunfish 96-h LC₅₀ 3.4 mg/L; Rainbow trout 96-h LC₅₀ 3.2 mg/L.

Use classification: Not available.

Synthesis and Analytical Methods

Synthesis: Not available.

Purification of technical: Not available.

Analytical methods: Not available.

Historical: U.S. patent 4,988,384 was issued to Monsanto. Thiazopyr was purchased by Rohm and Haas in 1994.

Information Sources

Primary industry sources: Monsanto, and DowAgro Sciences..

References

1. Armbruster, B. L. et al. 1991. Pestic. Biochem. Physiol. 40:58.
2. Vaughn and Lehnen. 1991. Weed Sci. 39:450.

TRICLOPYR

[(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid

Nomenclature

Common name: triclopyr (ANSI, BSI, ISO, WSSA).

Manufacturers, products, and formulations

Dow AgroSciences: GARLON™ 3A, GRAND-STAND®, and TURFLON™ AMINE, 360 g ae/L (3 lb ae/gal), triethylamine (tea) salt, SL; GARLON 4, REMEDY™, and TURFLON ESTER, 480 g ae/L (4 lb ae/gal), butoxyethyl ester (be ester), EC; PATHFINDER II, 90 g ae/L (0.75 lb ae/gal), be ester, EC; ACCESS, mix of triclopyr be ester + picloram isooctyl ester at 240 + 120 g ae/L (2 + 1 lb ae/gal), EC; REDEEM® and CONFRONT™, mix of triclopyr + clopyralid at 270 + 90 g ae/L (2.25 + 0.75 lb ae/gal), tea salts, SL; CROSSBOW™ and TURFLON D, mix of 2,4-D + triclopyr at 240 + 120 g ae/L, be ester, EC; TURFLON II, mix of triclopyr tea salt + 2,4-D dimethylamine salt at 128 + 333 g ae/L (1.07 + 2.78 lb ae/gal), SL.

Monterey: TURFLON ESTER, 480 g ae/L, be ester, EC.

Platte: CHASER®, mix of 2,4-D + triclopyr at 240 + 120 g ae/L, be esters, EC.

Other names: DOWCO 233; 3,5,6-trichloro-2-pyridinyl-oxyacetic acid (IUPAC); (3,5,6-trichloro-2-pyridyloxy)acetic acid.

Chemical family: Pyridinecarboxylic acid.

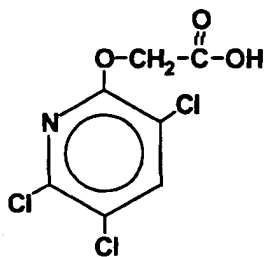
AWLN: Acid (6N) bO1VQ cG eG fG; Be ester (6N) bO1VO2O4 cG eG fG; Tea salt (6N) bO1VQ cG eG fG & 1J1&1.

CAS number: Acid 55335-06-3; Be ester 64700-56-7; Tea salt 57213-69-1.

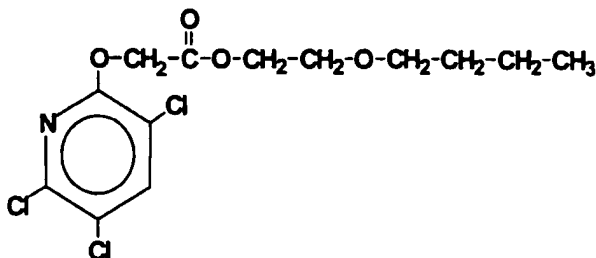
Chemical and Physical Properties

Chemical structure

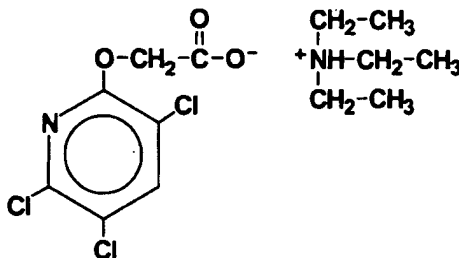
Acid



Butoxyethyl (butotyl) ester



Triethylamine (triethylammonium) salt



Molecular formula: Acid $C_7H_4Cl_3NO_3$; Butoxyethyl ester (Be ester) $C_{13}H_{16}Cl_3NO_4$; Triethylamine (Tea) salt $C_{13}H_{19}Cl_3N_2O_3$.

Molecular weight: Acid 256.47; Be ester 356.63; Tea salt 357.66.

Description: Fluffy white solid.

Density: 1.85 g/mL

Melting point: 148-150°C

Boiling point: Decomposes before boiling.

Vapor pressure: 1.6×10^{-7} kPa (1.26×10^{-6} mm Hg) at 25°C, 7×10^{-7} kPa (5.30×10^{-6} mm Hg) at 40°C, 10^{-6} kPa (1.03×10^{-5} mm Hg) at 50°C, and 1.3×10^{-5} kPa (1.04×10^{-4} mm Hg) at 70°C.

Stability: Decomposed by UV light; Decomposes at 290°C.

Solubility

Acid

water 430 mg/L at 25°C

organic solvents g/100 mL at 25°C:

acetone 98.9

ethanol soluble

acetonitrile 12.6

n-hexane 0.041

benzene 2.73

n-octanol 30.7

chloroform 2.73

xylene 2.79

Butoxyethyl ester

water 23 mg/L at 25°C (ref. 5)

Triethylamine salt

water 2,100,000 mg/L at 25°C (ref. 5)

pK_a: 2.68**K_{ow}:** 2.64 at pH 5, 0.36 at pH 7, and 0.11 at pH 9.**Herbicidal Use**

Triclopyr can be foliar-applied at 1.12-10.1 kg ae/ha (1-9 lb ae/A) or in a spray-to-wet application at 0.44-0.89 kg ae in 100-400 L (1.5-3 lb ae in 100-400 gal) of total spray in noncrop land areas such as utility and pipeline rights-of-way, roadsides, railroads, industrial sites, certain forestry sites, rangeland, and permanent pastures. It can be applied POST at 0.56-1.12 kg ae/ha (0.5-1 lb ae/A) in turf, and POST at 0.28-0.42 kg ae/ha (0.25-0.375 lb ae/A) in rice. Triclopyr also can be applied directed-POST for conifer release, injected into stem cuts for controlling large trees, applied to freshly cut stumps, and mixed with oil for bark treatment on young trees. It controls many annual broadleaf weeds including black medic, clover spp., dandelion, ground ivy, burdock, and plantain spp., as well as many tree and brush species. A nonionic surfactant is required in water applications for maximum efficacy.

Use Precautions

Fire hazard: GARLON 4, REMEDY, and TURFLON ES-TER are combustible but nonflammable; flash points are 64°C (147°F) (TCC). GARLON 3A and TURFLON AMINE are nonflammable; flash points are 43°C (110°F).

Corrosiveness: Slightly corrosive to aluminum on extended exposure.

Storage stability: Stable for >2 yr. Store above 2°C (36°F) to prevent crystallization, or agitate before use.

Cleaning glassware/spray equipment: Detergent wash and rinse with water.

Emergency exposure: Flush eyes or skin with water. If GARLON 3A or GARLON 4 are ingested, do not induce vomiting; seek medical assistance.

Incompatibilities: Formulated products are incompatible with oxidizing substances, acid, and base.

Behavior in Plants

Symptomology: Symptoms are typical of other auxin-type herbicides, and include epinastic bending and twisting of stems and petioles, stem swelling (particularly at nodes) and elongation, and leaf cupping and curling. Leaf shape and venation often appear abnormal. This is followed by chlorosis at the growing points, growth inhibition, wilting, and necrosis. Death of susceptible plants occurs slowly, usually within 3-5 wk. At low concentrations, young leaves may appear puckered and the tips of new leaves may develop into narrow extensions of the midrib.

Absorption: Triclopyr readily penetrates foliage, with a rain-free period of 4 h required for maximum efficacy. The

butoxyethyl ester is absorbed by leaves particularly rapidly. Uptake into wheat and barley leaves was essentially complete 12 h after treatment (3). However, foliar penetration in chickweed, a susceptible species, was considerably slower and less complete than in wheat or barley. Triclopyr also is readily absorbed by roots.

Translocation: Rapidly transported in plants, primarily via the symplastic pathway (including the phloem), and accumulating at the growing points (4). Between 40 and 67% of triclopyr penetrating the foliage of barley, wheat, and chickweed moved out of the treated leaf within 3 d of application (3). About 3.6% of foliar-applied triclopyr accumulated in the roots of horsenettle (2). Root-absorbed triclopyr appears to translocate to shoots.

Mechanism of action: Not completely understood, but similar to that of endogenous auxin (IAA) and other auxin-type herbicides. The specific cellular or molecular binding site relevant to the action of IAA and the auxin-type herbicides has not been identified. Nevertheless, the primary action of these compounds appears to involve cell wall plasticity and nucleic acid metabolism. Triclopyr is thought to acidify the cell wall by stimulating the activity of a membrane-bound ATPase proton pump. The reduction in apoplastic pH induces cell elongation by increasing the activity of enzymes responsible for cell wall loosening. Low concentrations of triclopyr also stimulate RNA polymerase, resulting in subsequent increases in RNA, DNA, and protein biosynthesis. Abnormal increases in these processes presumably lead to uncontrolled cell division and growth, which results in vascular tissue destruction. In contrast, high concentrations of triclopyr and other auxin-type herbicides inhibit cell division and growth, usually in meristematic regions that accumulate photosynthate assimilates and herbicide from the phloem. Triclopyr and other auxin-type herbicides stimulate ethylene evolution which may in some cases produce the characteristic epinastic symptoms associated with exposure to these herbicides.

HRAC/ WSSA Group Designation: HRAC - O/ WSSA - 4.

Metabolism in plants: Triclopyr esters are rapidly hydrolyzed to the triclopyr acid. While metabolism of the acid may be slow in some plants (2, 4), it appears to be rapid in others, particularly in tolerant cereals (3). Both barley and wheat metabolized at least 85% of the acid and ester forms of triclopyr by 3 d after application. Metabolites included a mixture of unidentified water-soluble sugar conjugates, as well as an aspartate conjugate and a methyl ester. In chickweed, a glutamate conjugate also was identified.

Non-herbicidal biological properties: None known.

Mechanism of resistance in weeds: No known cases of resistance.

Behavior in Soil

Sorption: Not strongly adsorbed; varies with soil OM and clay content.

K_{oc}: Average is 20 mL/g (estimated) for the triethylamine salt and 780 mL/g for the butoxyethyl ester (5).

Transformation

Photodegradation: Rapidly degraded; laboratory half-life is 2–6 h in water. Rapidly degraded by photolysis in water with a half-life of 10 h at 25°C, producing trichloropyridinol as the major metabolite.

Other degradation: Degraded by microbes.

Persistence: Triclopyr is moderately persistent with an average half-life of 30 d, ranging from 10–46 d depending on soil type, moisture, and temperature.

Mobility: Not available.

Volatilization: Negligible losses.

Toxicological Properties

Toxicity tests were conducted with technical grade triclopyr acid unless otherwise indicated.

Acute toxicity

Triclopyr acid technical: Oral LD₅₀ rat 713 mg/kg; Dermal LD₅₀ rabbit >2000 mg/kg; 4-h Inhal. LC₅₀ NAV; Skin irrit. rabbit, none; Skin sensitiz. guinea pig, positive in conc. solution, negative in dilute solution; Eye irrit. rabbit, mild.

GARLON 3A: Oral LD₅₀ male rat 2574 mg/kg; Dermal LD₅₀ rabbit >5000 mg/kg; 4-h Inhalation LC₅₀ > 2.6 mg/kg; Eye irrit. rabbit, severe.

GARLON 4: Oral LD₅₀ male rat 1581 mg/kg; Dermal LD₅₀ rabbit >2000 mg/kg; 4-h Inhalation LC₅₀ > 5.2 mg/l; Skin irritation rabbit, moderate; Skin sensitizing guinea pig, positive in concentrated solution, negative in dilute solution; Eye irrit. rabbit, slight.

Subchronic toxicity

90-d dietary, rate: NOEL 5 mg/kg/d; decreased body weight gain at >50 mg/kg/d and kidney effects at >20 mg/kg/d..

1-yr dietary, dog: NOEL 5 mg/kg/d.

Chronic toxicity

22-mo dietary, mouse: NOEL 5.3 mg/kg/d; not oncogenic.

24-mo dietary, rat: NOEL 3 mg/kg/d; not oncogenic.

Teratogenicity

Ra: NOEL 50 mg/kg/day (fetal and maternal eval.); not teratogenic.

Rabbit: NOEL 75 mg/kg/day (fetal) and 25 mg/kg/day (maternal); not teratogenic.

Reproduction

Rat: NOEL 25 mg/kg/d; NOEL 5 mg/kg/d (paternal); not a selective reproductive toxin.

Mutagenicity: *In vitro* and *in vivo* tests indicate no mutagenic potential.

Wildlife

Triclopyr acid technical: Bobwhite quail 8-d dietary LC₅₀ 2934 ppm; Japanese quail 8-d dietary LC₅₀ 3272 ppm; Mallard duck, oral LD₅₀ 1698 mg/kg, 8-d dietary LC₅₀ >5620 ppm; Honey bee topical LD₅₀ >100 µg/bee; Daphnia 48-h

LC₅₀ 133 mg/L; Bluegill sunfish 96-h LC₅₀ 148 mg/L; Rainbow trout 96-h LC₅₀ 117 mg/L.

Triclopyr butoxyethyl ester technical: Bobwhite quail 8-d dietary LC₅₀ 5401 ppm; Mallard duck, 8-d dietary LC₅₀ > 5401 ppm; Honey bee topical LD₅₀ >100 µg/bee; Daphnia 48-h LC₅₀ 1.7 mg/L; Bluegill sunfish 96-h LC₅₀ 0.36 mg/L; Rainbow trout 96-h LC₅₀ 0.65 mg/L.

Triclopyr triethylamine salt technical: Bobwhite quail 8-d dietary LC₅₀ >10,000 ppm; Mallard duck, oral LD₅₀ 3176 mg/kg, 8-d dietary LC₅₀ >10,000 ppm; Honey bee topical LD₅₀ > 100 µg/bee; Daphnia 48-h LC₅₀ 775 mg/L; Bluegill sunfish 96-h LC₅₀ 891 mg/L; Rainbow trout 96-h LC₅₀ 613 mg/L.

Use classification: General Use for all products.

Synthesis and Analytical Methods

Synthesis: Not available.

Purification of technical: Not available.

Analytical methods: Residue analysis in water, soil, and leaf samples is done by GC with limits of detection as low as 10 ppb.

Historical: First reported in 1975 (1). Introduced by Dow Chemical Co.

Information Sources

Primary industry source: Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, IN 46268-1054..

References

1. Byrd, B. C. et al. 1975. Proc. West. Soc. Weed Sci. 28:44.
2. Gorrell, R. M. et al. 1988. Weed Sci. 36:447.
3. Lewer and Owen. 1990. Pestic. Biochem. Physiol. 36:187.
4. Radosevich and Bayer. 1979. Weed Sci. 27:22.
5. USA EPA Registration Eligibility Decision (RED). Triclopyr October 1998. EPA 738-R-98-011.
6. Wauchope, R. D. et al. 1992. Rev. Environ. Contam. Toxicol. 123:1.

DIQUAT

6,7-dihydrodipyrido[1,2- α :2',1'-c]pyrazinediium ion

Nomenclature

Common name: diquat (ANSI, BSI, ISO, WSSA).

Manufacturers, products, and formulations

Applied Biochemists: WEEDTRINE®-D, 48 g cation/L (0.4 lb cation/gal), dibromide salt, SL.

Syngenta: REGLONE®, 240 g cation/L (2 lb cation/gal), dibromide salt, SL; REWARD, 2 lb cation/gal.

Other names: AQUACIDE; Deiquat (Germany); DEXTRONE; FB/2; REGLONE; 1,1'-ethylene-2,2'-bipyridylium (IUPAC); 1,1'-ethylene-2,2'-bipyridylium ion; 6,7-dihydrodipyrido[1,2- α :2',1'-c]pyrazinediium dibromide salt; 6,7-dihydrodipyrido[1,2- α :2',1'-c]pyrazine-5,8-di-ium (IUPAC); 9,10-dihydro-8a-,10a-diazoniaphenanthrene (IUPAC).

Chemical family: Bipyridilium (dipyridilium).

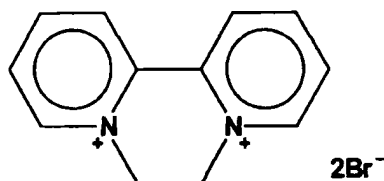
AWLN: Cation (b666 gK* jK@\$@); Dibromide salt (b666 gK* jK* @\$@) .E2.

CAS number: Cation 2764-72-9; Dibromide salt 85-00-7.

Chemical and Physical Properties

Chemical structure

Diquat dibromide salt



Molecular formula: Cation $C_{12}H_{12}N_2$; Dibromide salt $C_{12}H_{12}Br_2N_2$.

Molecular weight: Cation 184.24; Dibromide salt 344.05.

Description: Yellow crystalline solid (pure salt monohydrate).

Density: 1.61 g/mL at 25°C

Melting point: 325°C

Boiling point: Unknown.

Vapor pressure: <0.013 mPa (<<10⁻⁸ mm Hg) at 25°C

Stability: Degraded by UV light; Decomposes above 300°C; Decomposes in alkaline solution, but is stable in neutral or acidic solution.

Solubility

water 718,000 mg/L at 20°C and pH 7.2

organic solvents g/100 mL at 20°C:

acetone <0.01 ethanol slightly soluble

benzene insoluble n-hexane 0.01

chloroform insoluble

diethyl ether insoluble

methanol slightly soluble

toluene <0.01

pK_a: None (does not dissociate).

K_{ow}: 0.000055 at 20°C

Herbicidal Use

Diquat can be applied POST spray-to-wet using 240 g cation/100 L water (2 lb cation/100 gal water) to control cattails. Diquat also can be applied to ponds, lakes, and drainage ditches for control of algae, submersed aquatic weeds such as bladderwort, coontail, and Elodea, and floating aquatic weeds such as pennywort, salvinia, and water hyacinth. Can be used as a potato desiccant and non-selective weed control in non-crop areas.

Use Precautions

Fire hazard: DIQUAT is aqueous and nonflammable.

Corrosiveness: Dilute spray solutions of DIQUAT are noncorrosive to all materials commonly used in spray equipment; concentrated solutions corrode aluminum rapidly. Undiluted diquat should not be stored in contact with metals.

Storage stability: Stable at 54°C for 14 d. Shelf life is indefinite under normal storage conditions. Diquat technical is somewhat sensitive to UV light. The product is stable to heat beyond ordinary ambient temperatures. The solution does not crystallize at 0°C (32°F).

Cleaning glassware/spray equipment: Flush equipment with water.

Emergency exposure: If ingested, induce vomiting and get medical attention immediately. Perform gastric lavage and give repeated suspensions of activated charcoal together with saline purgatives. Removal of diquat from the blood requires prolonged charcoal hemoperfusion.

Incompatibilities: Incompatible with some alkyl sulfonate or alkyl aryl sulfonate wetting agents or alkali metal salts of hormone weed killers. Diquat may hydrolyze in the presence of alkaline materials including alkaline water. DIQUAT may be mixed with 2,4-D, substituted ureas, uracils, dalapon, and s-triazines.

Behavior in Plants

Symptomology: Rapid wilting and desiccation beginning within several h of application in full sunlight. Complete foliar necrosis occurs in 1-3 d.

Absorption/translocation: Rapidly absorbed into leaves and is rainfast within 1 to 2 h. More than 50% of applied diquat

was absorbed by leaves of three species within 1 h (1). Diquat translocates in the apoplast, but rapid cell death following absorption along with the normal upward movement of xylem flow usually prevents appreciable translocation from treated leaves. Under certain conditions favoring downward xylem movement, diquat may translocate out of treated leaves and into roots of potatoes. Diquat is tightly adsorbed to negatively charged leaf surfaces and membranes due to its positive charge and highly polar nature.

Mechanism of action: Diquat accepts electrons from photosystem I and is reduced to form the diquat radical, which in turn reduces molecular oxygen to form superoxide radical. Superoxide then reacts with itself in the presence of superoxide dismutase to form hydrogen peroxide. Hydrogen peroxide and superoxide react to generate hydroxyl radical. Superoxide and, to a lesser extent, hydrogen peroxide may oxidize SH groups on various organic compounds within the cell. Hydroxyl radical, however, is extremely reactive and readily destroys unsaturated lipids, including membrane fatty acids and chlorophyll. Hydroxyl radical produces lipid radicals which react with oxygen to form lipid hydroperoxides plus another lipid radical to initiate a self-perpetuating chain reaction of lipid oxidation. Such lipid hydroperoxides destroy the integrity of cell membranes allowing cytoplasm to leak into intercellular spaces which leads to rapid leaf wilting and desiccation. Diquat can be reduced/oxidized repeatedly (2).

HRAC/ WSSA Group Designation: HRAC - D/ WSSA - 22.

Metabolism in plants: Diquat apparently is not metabolized in higher plants, although it can be photodegraded on plant surfaces (4).

Non-herbicidal biological properties: No fungicide, nematocide, or insecticide activity. Diquat is highly toxic to mammals.

Mechanism of resistance in weeds: Most paraquat-resistant biotypes are resistant to diquat, although often at substantially reduced levels. High levels of diquat resistance have occurred in biotypes of capeweed (*Arctotheca calendula*) and horseweed. Resistance mechanisms have not been determined, but may be similar to the protective or sequestration mechanisms proposed for paraquat resistance (3).

Behavior In Soil

Sorption: Extremely tightly adsorbed to (negatively-charged) soil particles due to its dicationic nature. Diquat is primarily adsorbed to clay, less so to OM. Diquat bound to soil is unavailable for plant uptake and is largely unavailable to soil microbes.

K_{oc}: Average is 1,000,000 mL/g (estimated) (5).

Transformation

Photodegradation: Losses probably occur on sprayed leaf surfaces and on dead and decaying vegetation. Photochemical decomposition of diquat has been measured in the lab by irradiating thin layers of soil, but has not been unequivocally demonstrated under field conditions.

Other degradation: Certain microbe species in soil-less culture media decompose diquat. However, they degrade

diquat bound to soil slowly or not at all.

Persistence: Typical half-life is 1000 d (5). Diquat is highly persistent due to strong binding to clay and unavailability to microbes. Diquat in soil is not taken up by plants, so any crop can be seeded at any time after application.

Mobility: Immobile in soil.

Volatilization: No losses.

Toxicological Properties

Toxicity tests were conducted with technical grade diquat dibromide salt unless otherwise indicated.

Acute toxicity

Diquat dibromide salt technical: Oral LD₅₀ rat 230 mg/kg, mouse 125 mg/kg, dog 100-200 mg/kg, cow 30 mg/kg; Dermal LD₅₀ rabbit >400 mg/kg; 4-h Inhal. LC₅₀ NAV; Skin irrit., NAV; Skin sensitiz., NAV; Eye irrit., NAV.

Subchronic toxicity: Not available.

Chronic toxicity

18-mo dietary, mouse: NOEL NAV; not carcinogenic.

24-mo dietary, rat: NOEL 25 ppm; cataracts after ~100 wk at 36 ppm; not oncogenic at 36 mg/kg/d; not carcinogenic.

12-mo dietary, dog: NOEL 50 ppm; cataracts after 15 mo at 150 ppm; not carcinogenic.

Teratogenicity: Not available.

Reproduction

Rat: NOEL NAV; not a reproductive toxin; growth retardation at 25 mg/kg/d.

Mutagenicity: Not available.

Wildlife

Diquat dibromide salt technical: Hen oral LD₅₀ 200-400 mg/kg; Partridge oral LD₅₀ 295 mg/kg; Mirror carp 96-h LC₅₀ 67 mg/L; Rainbow trout 96-h LC₅₀ 21 mg/L.

Use classification: General Use.

Synthesis and Analytical Methods

Synthesis: 2,2'-bipyridyl is reacted with di-*n*-propyl amine.

Purification of technical: Recrystallization from water or aqueous solvent mixtures. Diquat dibromide monohydrate may be isolated from the formulated product as follows: Slightly acidify with hydrobromic acid. Add 10 volumes of acetone to each volume of the diquat formulation and stir vigorously. Filter and rinse the yellow solid diquat dibromide monohydrate with acetone. Further purify by dissolving the precipitate in a minimum of water, acidifying with hydrobromic acid, and repeating the precipitation with 10 volumes of acetone.

Analytical methods: Methods for formulated product and residue analysis are available (6), and are based on spectrophotometric measurement.

Historical: First made by Dyestuffs Division of I.C.I., Ltd.

First used in 1955 as a growth regulator. British patent 785,732 was applied for in 1955.

Information Sources

Primary industry source: Syngenta.

References

1. Brian, R. C. 1967. *Ann. Appl. Biol.* 59:91.
2. Dodge, A. D. 1982. Pages 57-77 in D. E. Moreland, J. B. St. John, and F. D. Hess, eds., *Biochemical Responses Induced by Herbicides*. Am. Chem. Soc. Symp. Ser. No. 181, Washington, D.C.

3. Dodge, A. D. 1991. Pages 165-176 in J. C. Caseley, G. W. Cussans, and R. K. Atkin, eds., *Herbicide Resistance in Weeds and Crops*. Butterworth-Heinemann, Oxford.
4. Funderburk and Lawrence. 1964. *Weeds* 12:259.
5. Wauchope, R. D. et al. 1992. *Rev. Environ. Contam. Toxicol.* 123:1.
6. Zweig, G., ed. 1967. *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives*, Vol. 5. Academic Press, New York.

DITHIOPYR

S,S-dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarbothioate

Nomenclature

Common name: Dithiopyr (ANSI, ISO, WSSA).

Manufacturers, products, and formulations

Dow Agro: DIMENSION, 119.8 g ai/L (1 lb ai/gal), EC; DIMENSION 0.1G, 0.1% ai; DIMENSION 0.25G, 0.25% ai, GR; STAKEOUT 1G, 1% ai, GR.

Other names: MON 7200; MON 15100; MON 15151; RH-101664; 3,5-pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-*S,S*-dimethylester; *S,S'*-dimethyl-2-difluoromethyl-4-isobutyl-6-trifluoromethylpyridine-3,5-dicarbothioate.

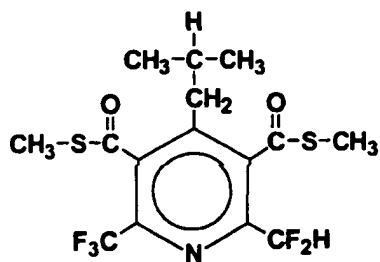
Chemical family: Pyridine.

AWLN: (6N) bYFF cVSI d1Y1&1 eVSI fXFFF

CAS number: 97886-45-8

Chemical and Physical Properties

Chemical structure



Molecular formula: $C_{15}H_{16}F_5NO_2S_2$

Molecular weight: 401.41

Description: Crystalline, colorless, faint odor.

Density: 1.42 g/mL at 20°C

Melting point: 65°C

Boiling point: 52°C at 760 mm Hg

Vapor pressure: 0.53 mPa (4×10^{-6} mm Hg) at 25°C

Stability: >2 yr at >0°C

Solubility: water 1.38 mg/L at 20°C

pK_a: None.

K_{ow}: 56,250

Herbicidal Use

Dithiopyr is applied PRE at 0.056-0.56 kg ai/ha (0.05-0.5 lb ai/A) or POST at 0.14-0.56 kg ai/ha (0.125-0.5 lb ai/A) in direct-seeded and transplanted rice; PRE at 0.14-0.56 kg ai/ha or POST at 0.56 kg ai/ha in established turf [maximum single application to turf is 0.56 kg ai/ha with total amount not to exceed 1.68 kg ai/ha (1.5 lb ai/A)]; and PRE at 0.14-2.24 kg ai/ha (0.125- 2 lb ai/A) in ornamentals, trees, and other perennial crops. Dithiopyr controls several annual grass and small-seeded broadleaf weeds such as barnyardgrass, crabgrass spp., goosegrass, *Oxalis*, and spurge.

Use Precautions

Fire hazard: Technical and DIMENSION EC are nonflammable; flash points are 84°C (183°F) and 63°C (145°F), respectively.

Corrosiveness: Copper, iron, and zinc were not corroded after a 2-wk exposure to DIMENSION EC in sunlight at 52°C (126°F).

gill sunfish 96-h LC₅₀ 0.2 mg/L; Channel catfish 96-h LC₅₀ 0.4 mg/L; Minnow reproduction MAC >0.038 <0.074 mg/L; Rainbow trout 96-h LC₅₀ 0.4 mg/L; Eastern oyster LC₅₀ 0.095 mg/L; Fiddler crab LC₅₀ >1000 mg/L; Freshwater clam LC₅₀ 10 mg/L; Grass shrimp LC₅₀ 0.032 mg/L.

Use classification: General Use.

Synthesis and Analytical Methods

Synthesis: React 3,4-dichlorobenzotrifluoride and resorcinol. The resulting intermediate is nitrated and then ethoxylated to produce oxyfluorfen.

Purification of technical: Proprietary.

Analytical methods: Available from DowAgro Sciences.

Historical: First reported in 1975 (6). Introduced by Rohm and Haas Company; U.S. patent 3,798,276. First registration occurred in 1976, although first U.S. registration was in 1979.

Information Sources

Primary industry source: DowAgro Sciences.

References

1. Duke, S. O. et al. 1991. *Weed Sci.* 39:465.
2. Fadayomi and Warren. 1977. *Weed Sci.* 25:97.
3. Fadayomi and Warren. 1977. *Weed Sci.* 25:111.
4. Lee and Duke. 1994. *Abstr. Weed Sci. Soc. Am.* 34:52.
5. Wauchope, R. D. et al. 1992. *Rev. Environ. Contam. Toxicol.* 123:1.
6. Yih and Swithenbank. 1975. *J. Agric. Food Chem.* 23:592.

PARAQUAT

1,1'-dimethyl-4,4'-bipyridinium ion

Nomenclature

Common name: paraquat (ANSI, BSI, ISO, WSSA).

Manufacturers, products, and formulations

Griffin LLC: BOA®, 2.5 lb ai/gal, SL.

Syngenta: CYCLONE®, 240 g cation/L (2 lb cation/gal), dichloride salt, SL; GRAMOXONE® MAX, 360 g cation/L, dichloride salt, SL; GRAMOXONE EXTRA and CYCLONE CF, 300 g cation/L (2.5 lb cation/gal), dichloride salt, SL; STARFIRE®, 180 g cation/L (1.5 lb cation/gal), dichloride salt, SL.

Other names: CEKUQUAT; DEXTRONE; DEXURON; ESGRAM; GOLDQUAT 276; HERBAXON; HERBAXONE; methyl viologen; PAQUAT; PILLARQUAT; PILLARXONE; PP 148; SWEEP; TOTAL; TOXER; WEEDOL.

Chemical family: Bipyridilium (dipyridilium).

AWLN: Cation (6K*) a1 d-d(6K*) a1; Dichloride salt (6K*)

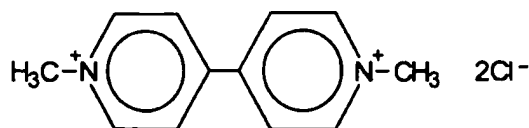
a1 d-d(6K*) a1 .G2.

CAS number: Cation 4685-14-7; Dichloride salt 1910-42-5.

Chemical and Physical Properties

Chemical structure:

Paraquat dichloride salt



Molecular formula: Cation C₁₂H₁₄N₂; Dichloride salt C₁₂H₁₄Cl₂N₂.

Molecular weight: Cation 186.26; Dichloride salt 257.16.

Description: White crystalline solid.

Density: 1.5 g/mL at 25°C

Melting point: 340°C

Boiling point: Unknown.

Vapor pressure: <0.1 mPa (<10⁻⁷ mm Hg)

Stability: Degraded by UV light; Decomposes at ~300°C; Unstable in alkaline solution.

Solubility

water 620,000 mg/L at 25°C (ref. 8)

organic solvents at 25°C:

acetone slightly soluble hydrocarbons insoluble

carbon disulfide insoluble kerosene insoluble

ethanol insoluble

dimethylformamide slightly soluble

pK_a: None.

K_{ow}: 4.5 at 20°C

Herbicidal Use

Paraquat is a non-selective, foliar-applied herbicide, often used to control existing vegetation at planting in no-till. It can be applied preplant or PRE in many agronomic crops, vegetables, flowers, and fruits at rates ranging from 0.28-1.05 kg cation/ha (0.25-0.94 lb cation/A). Other uses include: dormant season in established alfalfa, clover, mint, and rhubarb; between cuttings at 0.28 kg cation/ha in established alfalfa; pre-harvest at 0.34-0.53 kg cation/ha (0.3-0.47 lb cation/A) in drybeans, sunflowers, guar, potatoes, and soybeans; POST-directed at 0.53 kg cation/ha (0.47 lb cation/A) in corn, sorghum, soybeans, sugarcane, pineapple, small fruits, cassavas, taniars, yams, pigeon peas, strawberries, trees and vines, guava, hops, tomatoes, and peppers; weed control in fallow (including Conservation Reserve and Federal Set-aside programs) and noncropland; and pre-harvest desiccation of potato vines and weed control in rubber and coffee plantations. A nonionic surfactant or oil adjuvant is required for maximum efficacy.

Use Precautions

Fire hazard: All products are aqueous and noncombustible. See Corrosiveness.

Corrosiveness: Paraquat corrodes aluminum, and in concentrated form may be slightly corrosive to certain other metals. Dilute spray-tank solutions generally are noncorrosive to most materials used in spray equipment. Paraquat and aluminum react to produce hydrogen gas which may form a highly combustible gas mixture. This gas could flash or explode if ignited.

Storage stability: Shelf life is indefinite under normal storage conditions. Dry technical paraquat is somewhat sensitive to UV light. All products are stable to heat beyond the range of ordinary room temperature. Store above 0°C (32°F).

Cleaning glassware/spray equipment: Flush equipment with water.

Emergency exposure: If ingested, immediately induce vomiting. Administer fluids and induce further vomiting. Seek immediate medical attention. Paraquat can be lethal if ingested in

small amounts and treatment must begin immediately.

Incompatibilities: Not compatible with some alkyl sulfonate or alkyl aryl sulfonate wetting agents or alkali-metal salts of hormone weed killers. Can hydrolyze in alkaline solution.

Behavior in Plants

Symptomology: Rapid wilting and desiccation beginning within several h of application in full sunlight. Complete foliar necrosis occurs in 1-3 d.

Absorption/translocation: Rapidly absorbed into foliage and is rainfast 30 min after application. Rapid foliar uptake requires a nonionic surfactant. More than 50% of applied paraquat was absorbed by leaf tissues of three species within 1 h (2). Paraquat translocates only in the apoplast (including the xylem), and thus foliar-applied paraquat remains in treated leaves under normal conditions. When soil moisture is low and relative humidity high, paraquat residues in desiccating potato vines may move to the tubers in response to basipetal xylem flow facilitated by water demands of the growing tubers.

Mechanism of action: Paraquat accepts electrons from photosystem I and is reduced to form the paraquat radical, which in turn reduces molecular oxygen to form superoxide radical. Superoxide then reacts with itself in the presence of superoxide dismutase to form hydrogen peroxide. Hydrogen peroxide and superoxide react to generate hydroxyl radical. Superoxide and, to a lesser extent, hydrogen peroxide may oxidize SH groups on various organic compounds within the cell. Hydroxyl radical, however, is extremely reactive and readily destroys unsaturated lipids, including membrane fatty acids and chlorophyll. Hydroxyl radical produces lipid radicals which react with oxygen to form lipid hydroperoxides plus another lipid radical to initiate a self-perpetuating chain reaction of lipid oxidation. Such lipid hydroperoxides destroy the integrity of cell membranes allowing cytoplasm to leak into intercellular spaces which leads to rapid leaf wilting and desiccation. Paraquat can be reduced/oxidized repeatedly (4).

HRAC/WSSA Group Designation: HRAC -D/ WSSA - 22.

Metabolism in plants: Paraquat apparently is not metabolized in higher plants. Paraquat remaining on the plant surface, however, is photodegraded about 25-50% in 3 wk of bright sunlight, producing *N*-methyl isonicotinic acid which later degrades to methylamine (6). Since plants are killed rapidly in bright sunlight, significant quantities of the breakdown products are formed only on the surface of dead tissues.

Non-herbicidal biological properties: Paraquat is highly toxic in mammalian systems. No insecticidal or nematocidal properties are known, although it can be used to control columnaris, a myxobacterial disease of fish.

Mechanism of resistance in weeds: Paraquat resistance has been confirmed in at least 12 species. The mechanism(s) of resistance is controversial and may be due to elevated activities of enzymes that protect against toxic effects of oxygen radicals (7) or to sequestration or exclusion of the herbicide from the target site (5).

Behavior in Soil

Sorption: Extremely rapidly and tightly adsorbed to soil, primarily to clay particles. The dicationic paraquat forms ionic bonds with negatively charged clays, even inserting into the layer planes of montmorillonite clay. Paraquat is completely inactive in soil.

K_{oc} : Estimated at 1,000,000 mL/g (8).

Transformation

Photodegradation: Can be degraded from desiccated plant surfaces and possibly from soil surfaces to the extent of 25-50% in 3 wk under bright sunlight.

Persistence: Highly persistent with an average field half-life estimated at 1000 d (8). However, paraquat residues are tightly adsorbed and biologically unavailable in soil.

Mobility: Completely immobile in soil due to extremely tight adsorption. No leaching potential.

Volatilization: Negligible losses.

Toxicological Properties

Toxicity tests were conducted with technical grade paraquat dichloride salt unless otherwise indicated.

Acute toxicity

Paraquat dichloride salt technical: Oral LD₅₀ male rat 112-150 mg/kg, monkey 50 mg/kg, cat 48 mg/kg, cow 50-75 mg/kg; Dermal LD₅₀ rabbit 240 mg/kg; 4-h Inhal. LC₅₀ rat nontoxic; Skin irrit. rabbit, yes; Skin sensitiz. guinea pig, no; Eye irrit., NAV.

GRAMOXONE EXTRA: Oral LD₅₀ rat 40-150 mg/kg; Dermal LD₅₀ rabbit 240 mg/kg; Skin irrit. rabbit, mild; Skin sensitiz. guinea pig, yes; Eye irrit. rabbit, severe.

CYCLONE: Oral LD₅₀ rat 40-150 mg/kg; Dermal LD₅₀ rabbit 240 mg/kg; Skin irrit. rabbit, mild (repeated exposure can cause skin damage, edema, and ulcerations); Skin sensitiz. guinea pig, yes; Eye irrit. rabbit, severe.

Subchronic toxicity: Not available.

Chronic toxicity

24-mo dietary, rat: NOEL 25 ppm; not carcinogenic.

24-mo dietary, dog: NOEL 34 mg/kg/d.

Teratogenicity: Not available.

Reproduction: Not available.

Mutagenicity: Not available.

Wildlife

Paraquat dichloride salt technical: Bobwhite quail oral LD₅₀ 981 mg/kg; Japanese quail oral LD₅₀ 970 mg/kg; Mallard duck oral LD₅₀ 4048 mg/kg; Rhode Island hen oral LD₅₀ 262 mg/kg; Brown trout 96-h LC₅₀ 2.5-13 mg/L; Rainbow trout 96-h LC₅₀ 32 mg/L.

Use classification: Restricted Use because of high mammalian toxicity.

Synthesis and Analytical Methods

Synthesis: Direct quaternization of 4,4'-bipyridyl with chloromethane under pressure with or without solvent. The iodide salt may be exchanged with the chloride salt or methylsulfate ion by use of ion exchange. Silver methylsulfate gives a quantitative exchange for the halide form.

Purification of technical: Paraquat dichloride may be isolated from the formulated product by adding gradually (with rapid stirring) 1 volume of paraquat formulation to 10-15 volumes of a 1:1 mixture of acetone:isopropanol. Filter and rinse the solid with acetone:isopropanol. Purify by dissolving the solid in a minimum amount of water and repeating the precipitation.

Analytical methods: Methods for formulated product analysis and residue analysis are available (Pages 475-481 in G. Zweig, ed. 1967. Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives, Vol. V. Academic Press, New York). Both methods are based on spectrophotometric measurement.

Historical: First synthesized by the Dyestuffs Division of ICI Ltd, and first used as a growth regulator in 1959. PP901 was the di(methyl sulfate) salt formulation. Herbicidal properties of the dichloride and bis(methyl sulfate) salts were described in 1958 (1), and their properties were reviewed in 1968 (3). Both salts were introduced by ICI Plant Protection Division; British patent 813,531.

Information Sources

Primary industry source: Syngenta.

References


1. Brian, R. C. 1958. Nature (London) 181:446
2. Brian, R. C. 1967. Ann. Appl. Biol. 59:91.
3. Calderbank, A. 1968. Adv. Pest Control Res. 8:127.
4. Dodge, A. D. 1982. Pages 57-77 in D. E. Moreland, J. B. St. John, and F. D. Hess, eds., Biochemical Responses Induced by Herbicides. Am. Chem. Soc. Symp. Ser. No. 181, Washington D.C.
5. Fuerst and Vaughn. 1990. Weed Technol. 4:150.
6. Funderburk and Lawrence. 1964. Weeds 12:259.
7. Shaaltiel and Gressel. 1986. Pestic. Biochem. Physiol. 26:22.
8. Wauchope, R. D. et al. 1992. Rev. Environ. Contam. Toxicol. 123:1.

Compendium of Pesticide Common Names

For purposes of trade, registration and legislation, and for use in popular and scientific publications, pesticides need names that are short, distinctive, non-proprietary and widely-accepted. Systematic chemical names are rarely short and are not convenient for general use, and so standards bodies assign common names to the active ingredients of pesticides. More than 1100 of these official pesticide names have been assigned by the International Organization for Standardization (ISO), in accordance with an established system of nomenclature.

This Compendium is believed to be the only place where all of the ISO-approved standard names of chemical pesticides are listed. It also includes approved names from national and international bodies for pesticides that do not have ISO names.

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Introduction	Browser requirements
Index of all common names	Index of non-ISO common names
Index of new common names	Index of updated data sheets
Index of IUPAC systematic names	Index of CAS systematic names
Index of molecular formulae	Index of CAS Registry Numbers®
Pesticide classification	Index of simple esters and salts
E-mail alerting service 	Naming of simple esters and salts
FAQ	Site map
Hints and Tips	Links
Copyright, Terms and Conditions	Accessibility (access keys)

Data sheets for new ISO common names are normally added within 2–3 weeks after meetings of ISO Technical Committee 81, which is responsible for ISO 1750.

Latest updates:

- August 2008 – added British pronunciations
- July 2008 – 3 new common names provisionally approved
- May 2008 – 3 new common names provisionally approved
- May 2008 – 24 common names published
- February 2008 – added a KLIC index of common names

- December 2007 – 262 common names approved
- December 2006 – 2 new common names provisionally approved

Search the Compendium for a common name



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The inclusion of a pesticide name in this Compendium must not be interpreted as a recommendation for the use of the substance in agriculture or in any other field.

It is essential to follow the instructions on the label before handling, storing or using any pesticide, and to comply with the requirements of the appropriate regulatory authority.

The information in this Compendium must not be used as a substitute for either Material Safety Data Sheets or labels on commercial pesticides.

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Compendium of Pesticide Common Names

Classified Lists of Pesticides

Acaricides	Algicides	Antifeedants
Avicides	Bactericides	Bird repellents
Chemosterilants	Fungicides	Herbicide safeners
Herbicides	Insect attractants	Insect repellents
Insecticides	Mammal repellents	Mating disrupters
Molluscicides	Nematicides	Plant activators
Plant growth regulators	Rodenticides	Synergists
Virucides	Miscellaneous	Chemical classes

These classified lists of pesticides include all of the compounds in the Compendium of Pesticide Common Names, of which there are more than 1500.

Each major group of pesticides (e.g. herbicides or plant growth regulators) is subdivided into chemical or other classes (e.g. chloroacetanilide herbicides or auxins).

As an aid to navigating the larger groups (acaricides, fungicides, herbicides, insecticides, nematicides and plant growth regulators), there are summaries containing just the chemical classes and not the individual substances.

Individual compounds can occur in more than one group or class, and at more than one place within a group or class.

Click the common name of any compound to see a data sheet with the status of the name, its IUPAC systematic name, its Chemical Abstracts systematic name and Registry Number, its molecular formula, and the group(s) and class(es) to which it belongs.

The CAB Thesaurus and the NAL Agricultural Thesaurus use a simplified version of this classification.

Classification by hazard

The classification used in the Compendium is based mainly on chemical structure and pesticidal activity, not on hazard. The World Health Organization produces a classification by hazard – The WHO Recommended Classification of Pesticides by

Hazard.

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A component of the Compendium of Pesticide Common Names

Compendium of Pesticide Common Names

Herbicides

- **amide herbicides**

- allidochlor
- amicarbazone
- beflubutamid
- benzadox
- benzipram
- bromobutide
- cafenstrole
- CDEA
- cyprazole
- dimethenamid
- dimethenamid-P
- diphenamid
- epronaz
- etnipromid
- fentrazamide
- flucarbazone
- flupoxam
- fomesafen
- halosafen
- isocarbamid
- isoxaben
- napropamide
- naptalam
- pethoxamid
- propyzamide
- quinonamid
- saflufenacil
- tebutam

- **anilide herbicides**

- chloranocryl
 - cisanilide
 - clomeprop
 - cypromid
 - diflufenican
 - etobenzanid
 - fenasulam
 - flufenacet
 - flufenican
 - ipfencarbazone
 - mefenacet
 - mefluidide
 - metamifop
 - monalide
 - naproanilide

pentanochlor

picolinafen

propanil

sulfentrazone

■ **arylalanine herbicides**

benzoylprop

flamprop

flamprop-M

■ **chloroacetanilide herbicides**

acetochlor

alachlor

butachlor

butenachlor

delachlor

diethatyl

dimethachlor

metazachlor

metolachlor

S-metolachlor

pretilachlor

propachlor

propisochlor

prynachlor

terbuchlor

thenylchlor

xylachlor

■ **sulfonanilide herbicides**

benzofluor

cloransulam

diclosulam

florasulam

flumetsulam

metosulam

perfluidone

pyrimisulfan

profluazol

○ **sulfonamide herbicides**

asulam

carbasulam

fenasulam

oryzalin

penoxsulam

pyroxsulam

see also sulfonylurea herbicides

○ **thioamide herbicides**

bencarbazone

chlorthiamid

● **antibiotic herbicides**

bilanafos

● **aromatic acid herbicides**

- **benzoic acid herbicides**
 - chloramben
 - dicamba
 - 2,3,6-TBA
 - tricamba
 - **pyrimidinyloxybenzoic acid herbicides**
 - bispyribac
 - pyriminobac
 - **pyrimidinylthiobenzoic acid herbicides**
 - pyrithiobac
- **phthalic acid herbicides**
 - chlorthal
- **picolinic acid herbicides**
 - aminopyralid
 - clopyralid
 - picloram
- **quinolinecarboxylic acid herbicides**
 - quinclorac
 - quinmerac
- **arsenical herbicides**
 - cacodylic acid
 - CMA
 - DSMA
 - hexaflurate
 - MAA
 - MAMA
 - MSMA
 - potassium arsenite
 - sodium arsenite
- **benzoylcyclohexanedione herbicides**
 - mesotrione
 - sulcotrione
 - tefuryltrione
 - tembotrione
- **benzofuranyl alkylsulfonate herbicides**
 - benfuresate
 - ethofumesate
- **benzothiazole herbicides**
 - benazolin
 - benzthiazuron
 - fenthiaprop
 - mefenacet
 - methabenzthiazuron
- **carbamate herbicides**
 - asulam
 - carboxazole
 - chlorprocarb
 - dichlormate
 - fenasulam
 - karbutilate

- terbucarb
- **carbanilate herbicides**
 - barban
 - BCPC
 - carbasulam
 - carbetamide
 - CEPC
 - chlorbufam
 - chlorpropham
 - CPPC
 - desmedipham
 - phenisopham
 - phenmedipham
 - phenmedipham-ethyl
 - propham
 - swep
- **cyclohexene oxime herbicides**
 - alloxydim
 - butroxydim
 - clethodim
 - cloproxydim
 - cycloxydim
 - profoxydim
 - sethoxydim
 - tepraloxym
 - tralkoxydim
- **cyclopropylisoxazole herbicides**
 - isoxachlortole
 - isoxaflutole
- **dicarboximide herbicides**
 - cinidon-ethyl
 - flumezin
 - flumiclorac
 - flumioxazin
 - flumipropyn
 - see also uracil herbicides
- **dinitroaniline herbicides**
 - benfluralin
 - butralin
 - dinitramine
 - ethalfluralin
 - fluchloralin
 - isopropalin
 - methalpropalin
 - nitralin
 - oryzalin
 - pendimethalin
 - prodiamine
 - profluralin
 - trifluralin

- **dinitrophenol herbicides**
 - dinofenate
 - dinoprop
 - dinosam
 - dinoseb
 - dinoterb
 - DNOC
 - etinofen
 - medinoterb
- **diphenyl ether herbicides**
 - ethoxyfen
 - **nitrophenyl ether herbicides**
 - acifluorfen
 - aclonifen
 - bifenox
 - chlomethoxyfen
 - chlornitrofen
 - etnipromid
 - fluorodifen
 - fluoroglycofen
 - fluronitrofen
 - fomesafen
 - furyloxyfen
 - halosafen
 - lactofen
 - nitrofen
 - nitrofluorfen
 - oxyfluorfen
- **dithiocarbamate herbicides**
 - dazomet
 - metam
- **halogenated aliphatic herbicides**
 - alorac
 - chloropon
 - dalapon
 - flupropanate
 - hexachloroacetone
 - iodomethane
 - methyl bromide
 - monochloroacetic acid
 - SMA
 - TCA
- **imidazolinone herbicides**
 - imazamethabenz
 - imazamox
 - imazapic
 - imazapyr
 - imazaquin
 - imazethapyr
- **inorganic herbicides**

- ammonium sulfamate
- borax
- calcium chlorate
- copper sulfate
- ferrous sulfate
- potassium azide
- potassium cyanate
- sodium azide
- sodium chlorate
- sulfuric acid
- **nitrile herbicides**
 - bromobonil
 - bromoxynil
 - chloroxynil
 - dichlobenil
 - iodobonil
 - ioxynil
 - pyraclonil
- **organophosphorus herbicides**
 - amiprofos-methyl
 - anilofos
 - bensulide
 - bilanafos
 - butamifos
 - 2,4-DEP
 - DMPA
 - EBEP
 - fosamine
 - glufosinate
 - glufosinate-P
 - glyphosate
 - piperophos
- **oxadiazolone herbicides**
 - dimefuron
 - methazole
 - oxadiargyl
 - oxadiazon
- **oxazole herbicides**
 - carboxazole
 - isouron
 - isoxaben
 - isoxachlortole
 - isoxaflutole
 - monisouron
 - pyroxasulfone
 - topramezone
- **phenoxy herbicides**
 - bromofenoxim
 - clomeprop
 - 2,4-DEB

2,4-DEP

difenopenten

disul

erbon

etnipromid

fenteracol

trifopsime

○ **phenoxyacetic herbicides**

4-CPA

2,4-D

3,4-DA

MCPA

MCPA-thioethyl

2,4,5-T

○ **phenoxybutyric herbicides**

4-CPB

2,4-DB

3,4-DB

MCPB

2,4,5-TB

○ **phenoxypropionic herbicides**

cloprop

4-CPP

dichlorprop

dichlorprop-P

3,4-DP

fenoprop

mecoprop

mecoprop-P

■ **aryloxyphenoxypropionic herbicides**

chlorazifop

clodinafop

clofop

cyhalofop

diclofop

fenoxaprop

fenoxaprop-P

fenthiaprop

fluazifop

fluazifop-P

haloxyfop

haloxyfop-P

isoxapyrifop

metamifop

propaquizafop

quizalofop

quizalofop-P

trifop

● **phenylenediamine herbicides**

dinitramine

- prodiamine
- **pyrazole herbicides**
 - azimsulfuron
 - difenzoquat
 - halosulfuron
 - metazachlor
 - pyrazosulfuron
 - pyroxasulfone
 - **benzoylpyrazole herbicides**
 - benzofenap
 - pyrasulfotole
 - pyrazolynate
 - pyrazoxyfen
 - topramezone
 - **phenylpyrazole herbicides**
 - fluazolate
 - nipyraclufen
 - pyraflufen
- **pyridazine herbicides**
 - credazine
 - pyridafof
 - pyridate
- **pyridazinone herbicides**
 - brompyrazon
 - chloridazon
 - dimidazon
 - flufenpyr
 - metflurazon
 - norflurazon
 - oxapyrazon
 - pydanon
- **pyridine herbicides**
 - aminopyralid
 - cliodinate
 - clopyralid
 - diflufenican
 - dithiopyr
 - flufenican
 - fluroxypyr
 - haloxydine
 - picloram
 - picolinafen
 - pyriclor
 - pyroxsulam
 - thiazopyr
 - triclopyr
- **pyrimidinediamine herbicides**
 - iprymidam
 - tioclorim
- **quaternary ammonium herbicides**

- cyperquat
- diethamquat
- difenzoquat
- diquat
- morfamquat
- paraquat
- **thiocarbamate herbicides**
 - butylate
 - cycloate
 - di-allate
 - EPTC
 - esprocarb
 - ethiolate
 - isopolinate
 - methiobencarb
 - molinate
 - orbencarb
 - pebulate
 - prosulfocarb
 - pyributicarb
 - sulfallate
 - thiobencarb
 - tiocarbazil
 - tri-allate
 - vernolate
- **thiocarbonate herbicides**
 - dimexano
 - EXD
 - proxan
- **thiourea herbicides**
 - methiuron
- **triazine herbicides**
 - dipropetryn
 - triaziflam
 - trihydroxytriazine
 - **chlorotriazine herbicides**
 - atrazine
 - chlorazine
 - cyanazine
 - cyprazine
 - eglinazine
 - ipazine
 - mesoprazine
 - procyazine
 - proglinazine
 - propazine
 - sebuthylazine
 - simazine
 - terbuthylazine
 - trietazine

- **methoxytriazine herbicides**
 - atraton
 - methometon
 - prometon
 - secbumeton
 - simeton
 - terbumeton
- **methylthiotriazine herbicides**
 - ametryn
 - aziprotryne
 - cyanatryn
 - desmetryn
 - dimethametryn
 - methoprotryne
 - prometryn
 - simetryn
 - terbutryn
- **triazinone herbicides**
 - ametridione
 - amibuzin
 - hexazinone
 - isomethiozin
 - metamitron
 - metribuzin
- **triazole herbicides**
 - amitrole
 - cafenstrole
 - epronaz
 - flupoxam
- **triazolone herbicides**
 - amicarbazone
 - bencarbazone
 - carfentrazone
 - flucarbazone
 - ipfencarbazone
 - propoxycarbazone
 - sulfentrazone
 - thiencarbazone
- **triazolopyrimidine herbicides**
 - cloransulam
 - diclosulam
 - florasulam
 - flumetsulam
 - metosulam
 - penoxsulam
 - pyroxsulam
- **uracil herbicides**
 - benzfendizone
 - bromacil
 - butafenacil

- flupropacil
- isocil
- lenacil
- saflufenacil
- terbacil
- **urea herbicides**
 - benzthiazuron
 - cumyluron
 - cycluron
 - dichloralurea
 - diflufenzopyr
 - isonoruron
 - isouron
 - methabenzthiazuron
 - monisouron
 - noruron
 - **phenylurea herbicides**
 - anisuron
 - buturon
 - chlorbromuron
 - chloreturon
 - chlorotoluron
 - chloroxuron
 - daimuron
 - difenoxuron
 - dimefuron
 - diuron
 - fenuron
 - fluometuron
 - fluothiuron
 - isoproturon
 - linuron
 - methiuron
 - methyldymron
 - metobenzuron
 - metobromuron
 - metoxuron
 - monolinuron
 - monuron
 - neburon
 - parafluron
 - phenobenzuron
 - siduron
 - tetrafluron
 - thidiazuron
 - **sulfonylurea herbicides**
 - **pyrimidinylsulfonylurea herbicides**
 - amidosulfuron
 - azimsulfuron
 - bensulfuron

- chlorimuron
 - cyclosulfamuron
 - ethoxysulfuron
 - flazasulfuron
 - flucetosulfuron
 - flupyrsulfuron
 - foramsulfuron
 - halosulfuron
 - imazosulfuron
 - mesosulfuron
 - nicosulfuron
 - orthosulfamuron
 - oxasulfuron
 - primisulfuron
 - pyrazosulfuron
 - rimsulfuron
 - sulfometuron
 - sulfosulfuron
 - trifloxysulfuron
- **triazinylsulfonylurea herbicides**
 - chlorsulfuron
 - cinosulfuron
 - ethametsulfuron
 - iodosulfuron
 - metsulfuron
 - prosulfuron
 - thifensulfuron
 - triasulfuron
 - tribenuron
 - triflusulfuron
 - tritosulfuron
- **thiadiazolylurea herbicides**
 - buthiuron
 - ethidimuron
 - tebuthiuron
 - thiazafluron
 - thidiazuron
- **unclassified herbicides**
 - acrolein
 - allyl alcohol
 - aminocyclopyrachlor
 - azafenidin
 - bentazone
 - benzobicyclon
 - buthidazole
 - calcium cyanamide
 - cambendichlor
 - chlorfenac
 - chlorfenprop
 - chlorflurazole

chlorflurenol
cinmethylin
clomazone
CPMF
cresol
cyanamide
ortho-dichlorobenzene
dimepiperate
endothal
fluoromidine
fluridone
flurochloridone
flurtamone
fluthiacet
indanofan
methyl isothiocyanate
OCH
oxaziclomefone
pentachlorophenol
pentoxazone
phenylmercury acetate
pinoxaden
prosulfalin
pyribenzoxim
pyriftalid
quinoclamine
rhodethanil
sulglycapin
thidiazimin
tridiphane
trimeturon
tripropindan
tritac

For a classification of herbicides according to their mode of action, developed by the Herbicide Resistance Action Committee and the Weed Science Society of America, please see: [Herbicide Classification According to Primary Sites of Action](#).

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A component of the Compendium of Pesticide Common Names